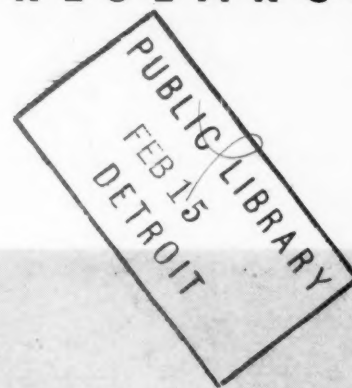


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U. S. DEPARTMENT OF COMMERCE
SINCLAIR WEEKS, Secretary
BUREAU OF PUBLIC ROADS
FRANCIS V. du PONT, Commissioner

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Evaluation of Air-Entraining Admixtures for Concrete

BY THE PHYSICAL RESEARCH BRANCH
BUREAU OF PUBLIC ROADS

Reported by FRANK H. JACKSON,¹ Chief, Non-Bituminous Section, and
ALBERT G. TIMMS, Supervising Highway Physical Research Engineer

This investigation was undertaken for the purpose of determining the acceptability of a number of commercial admixtures which were available at the time for use in the production of air-entrained portland cement concrete for highway pavements and bridges. The complete program involved the evaluation of 27 materials, each of which was tested in concrete to determine its ability to entrain air, as well as its effect on flexural and compressive strength and on durability. As the result of the evaluation study, 26 of the 27 materials which were received for test have been classified as acceptable for use as air-entraining admixtures.

PRIOR to 1950, information regarding the effectiveness of most of the materials available commercially for use in the production of air-entrained portland cement concrete, other than that furnished by the manufacturers themselves, was exceedingly meager and, as a result, the State highway departments and other users were reluctant to specify them. In fact, the only materials which were generally accepted prior to 1950 were the four which had been initially accepted by Committee C-1 of the American Society for Testing Materials under its standard procedure for evaluating additions for use in the manufacture of air-entraining portland cement.²

The term *addition* is generally understood to cover materials, other than gypsum, which are interground with portland cement clinker during the process of manufacturing the cement, while the term *admixture* is generally understood to cover those materials which are added to the concrete either prior to or during the mixing operation.

Although the A.S.T.M. acceptance procedure covered the use of the four materials only as additions, engineers in general have assumed that materials which are satisfactory for use in making air-entraining cement will also be satisfactory for use as admixtures in producing air-entrained concrete. Therefore, inasmuch as all four of these products were also being marketed as admixtures, they came to be generally accepted for this purpose.

The rapidly increasing use of air-entrained concrete during the past decade, and the consequently increasing demand for materials which

would entrain air, has resulted in the promotion of many new products, all claimed to be equal to or superior in air-entraining properties to the four which had been previously accepted. Very few data upon which to appraise these materials as air-entraining admixtures were available, however. It was to supply such data that the evaluation program described in this article was undertaken.³

Classification of Materials

As an initial step, a questionnaire was sent to all manufacturers of air-entraining admixtures known to the Bureau, together with a request for samples of their products. The purpose of the questionnaire was to obtain data regarding the nature of the materials, results of prior tests, extent of use, and field performance. This request resulted in the submission of 27 samples representing the products of 19 manufacturers. The materials have been classified with respect to their major constituents into seven groups, as follows:

- Group A.—Salts of wood resins.
- Group B.—Synthetic detergents.
- Group C.—Salts of sulfonated lignin.
- Group D.—Salts of petroleum acids.
- Group E.—Salts of proteinaceous materials.
- Group F.—Fatty and resinous acids and their salts.
- Group G.—Organic salts of sulfonated hydrocarbons.

Of the 27 materials submitted, seven were classified in group A, seven in group B, four in group C, two in group D, two in group E, four in group F, and one in group G. Seventeen of the samples were in liquid form, five were powders, four were in flake form, and one was a semisolid.

The classification of the individual materials into groups, the physical state in which each was received, and a brief statement of the probable source of each material and its essential chemical composition, are shown in table 1.

With the exception of the semisolid, which had to be neutralized, all of the admixtures had been neutralized prior to submission for test. They were added to the concrete in the physical state in which received except Nos. 7, 12, 13, 14, and 15, which were dissolved in water before use in order to insure uniform distribution in the mix.

Basis of Acceptance and Summary of Results

The criteria for acceptance which had been established by the Bureau provides that, when the admixture is used in an amount sufficient to entrain between 3 and 6 percent air in concrete of the proportions normally used for pavements and bridges:

1. The flexural and compressive strength of the concrete at the ages of 3 days, 28 days, and 1 year shall be not less than 88 percent of the strength of similar concrete of the same cement content and consistency but without the admixture, and
2. The durability of the concrete as measured by its resistance to alternate freezing and thawing in water, using a slow cycle of 24 hours, shall be substantially improved as compared to the durability of similar concrete of the same cement content and consistency but without the admixture.

As the result of the evaluation program, the Bureau has officially approved for use on Government contracts in the National Parks and National Forests, 26 of the 27 materials which were under consideration, including the 4 which previously had been accepted by the A.S.T.M. (see p. 278). One material met all of the required tests, but approval was deferred because the material, as submitted by the manufacturer, was not in suitable form for use as an admixture. Except for a few relatively minor deviations, the 27 admixtures met the 88-percent strength requirement at the three ages of test. They also complied with the requirement for durability, although in this respect the various materials differed considerably in performance. These differences could not be related directly to total air content, but it is possible that they were influenced by differences in the distribution or spacing of the air voids. This possibility is a subject for further study.

A detailed description of the test procedures employed in this work and a further discussion of the results follows.

Scope of Work and Materials Used

Three series of tests were conducted: Series I, a study of the effect of each of the 27 admixtures on the compressive and flexural strength of concrete, using a well-graded crushed limestone, 1½-inch maximum size, as coarse aggregate; Series II, a similar study using a siliceous gravel of identical size and grading as in Series I but covering only a selected group of 15 of the 27 admixtures; and Series III, a study of the effect

¹ Mr. Jackson retired on October 1, 1953.

² See A.S.T.M. tentative specification C 175-48T. The acceptance procedure outlined in this specification was withdrawn in 1950. The materials which had been accepted prior to withdrawal were known commercially as neutralized Vinsol resin, Darex AEA, N-Tair, and Airalon.

³ A companion article in this issue covers the chemical analysis of the same air-entraining admixtures that are considered here. The samples are identically numbered in both cases. In this article the samples are grouped according to source, but in the other study they are grouped according to treatment for chemical analysis.

Table 1.—Classification of admixtures

No.	Physical state	Probable source	Chemical constituents identified
GROUP A: SALTS OF WOOD RESINS			
1	Liquid	Pine wood stumps	Sodium soaps of wood resins.
2	do	do	do.
3	do	do	do.
4	do	do	do.
5	do	do	do.
6	do	do	Sodium and potassium soaps of wood resins.
7	Powder	do	Sodium soaps of wood resins.
GROUP B: SYNTHETIC DETERGENTS			
12	Flake	Synthesized from petroleum fractions	Alkyl aryl sulfonate and sodium sulfate.
13	do	do	do.
14	do	do	do.
15	do	do	do.
16	Liquid	do	Alkyl aryl sulfonate.
17	do	do	Alkyl aryl sulfonate and sodium sulfate.
26	do	Direct source uncertain ¹	Alkyl aryl sulfonate and proteinaceous material.
GROUP C: SALTS OF SULFONATED LIGNIN			
18	Powder	Byproduct of paper pulp industry ²	Calcium lignosulfonate. ³
20	do	do ²	Calcium lignosulfonate and calcium chloride. ³
21	do	do ²	do. ³
22	do	do ²	do. ³
GROUP D: SALTS OF PETROLEUM ACIDS			
11	Liquid	Petroleum refining processes	Sodium soaps of carboxylic acids (most likely naphthenic).
27	do	do	Sodium soaps of petroleum acids (possibly naphthenic) dissolved in petroleum oil.
GROUP E: SALTS OF PROTEINACEOUS MATERIALS			
24	Liquid	Animal hide industry	Calcium salts of complex proteinaceous acids.
25	do	do	do.
GROUP F: FATTY AND RESINOUS ACIDS AND THEIR SALTS			
8	Liquid	Byproduct of paper pulp industry ⁴	Sodium soaps of lignin, rosin, and fatty acids.
9	do	do ⁴	Triethanolamine and sodium soaps of lignin, rosin, and perhaps fatty acids.
10	do	do ⁴	Ammonium and sodium soaps of lignin and rosin along with appreciable unsaponified matter.
28	Semisolid	Byproduct of vegetable oil processing	Fatty acids and unsaponified matter.
GROUP G: ORGANIC SALTS OF SULFONATED HYDROCARBONS			
23	Liquid	Byproduct of petroleum refining processes	Triethanolamine salts of sulfonic acids.

¹ Analysis shows two major components present, separately derived from the animal hide industry and the petroleum industry.

² Acid process. ³ Stated to contain also a small quantity of alkyl aryl sulfonate. ⁴ Alkaline process.

of each of the 27 admixtures on durability, as measured by resistance to alternate freezing and thawing. In Series III the same coarse aggregate was used as in Series I, except that the maximum size was 1 inch. This maximum aggregate size was due to the smaller size specimen (3 by 4 by 16-inch) used in the freezing tests as compared with 6 by 6 by 21-inch beams and 6 by 12-inch cylinders used for strength tests.

Mix Proportions

The mix data for all series are given in tables 2 and 2A. For each series, two proportions were used, one for the base or reference mix without admixture and the other for the mixes containing entrained air. All mixes were designed to have a cement content of 6.0 ± 0.2 sacks of cement per cubic yard, with sufficient water to produce a

slump of approximately 3.0 inches. For each series, the actual weight of coarse aggregate per sack of cement was the same for both types of concrete. In the case of the air-entrained mixes, however, the quantity of sand was reduced in order to compensate for the volume of added air, thus maintaining a constant cement content. The reduction amounted to 20 pounds per sack of cement in the case of Series I, 17 pounds in the case of Series II, and 15 pounds in the case of Series III. The actual weights of aggregates per sack of cement are shown in table 2A.

In the case of Series I, the quantities of admixture used, air contents, and slumps are the average of three rounds of tests made on different days. For Series II, the corresponding values are the average of two rounds. In the case of Series III, the individual specimens were not cast separately but were sawed from slabs 16 by 24 by 4

inches in depth which were cast from single batches of concrete. The values shown for Series III in table 2 are, therefore, the results of tests on the single batches from which the slabs were cast.

The procedure for determining the proper quantity of admixture to use in each case was as follows:

For the first round of Series I, the first batch contained either the amount of admixture recommended by the manufacturer or the minimum of the recommended range, if so shown. If the resulting air content was within the 3- to 6-percent range set up as the criteria for acceptance, the batch was used. If the air content was within the range but close to either limit, the quantity of admixture for the second and third rounds was adjusted either up or down as needed to bring the air content closer to the middle of the permissible range. In the case of admixture 6, for example, 0.50 ounce of admixture per sack (the minimum of the recommended range) was used in round one. The resulting air content was 3.1 percent. Therefore, for the second and third rounds the quantity was increased to 0.63 ounce per sack, resulting in an air content of 3.8 percent for round two and 4.2 percent for round three. The average values for the three rounds were, therefore, 0.59 ounce of admixture per sack and 3.7 percent air content.

If the observed air content for the first batch was outside the limits of 3 to 6 percent, the batch was discarded and a new batch using an adjusted quantity of admixture was made. In the three cases where no recommendations were made by the manufacturers, trial batches were run to establish the correct quantities.

For Series II, the quantities of the admixtures were, in general, raised slightly as compared to the quantities used in Series I. This adjustment was made because of the lower sand content of the gravel mixes, experience having shown that without such correction the air contents in Series II would have been substantially lower than in Series I.

For Series III, it was decided to use the optimum quantity as determined in Series I. It was recognized that, because of the higher sand content of the mixes in Series III, the use of the same quantity of admixture would probably increase the air content. However, it was felt that some increase in air content would be justified in this mix due to the smaller maximum coarse aggregate size. As will be noted from table 2, the resulting air contents show considerable variation. They will be discussed in a later section of this report.

Fabrication of Specimens

A total of 10 mixing days was required to complete fabrication of the specimens for Series I. For each of the 27 admixtures, three specimens of a kind were cast on each of 3 mixing days—one for test at 3 days, one for test at 28 days, and one for test at 1 year. For the base mix, three specimens of a kind were cast on each of the 10 mixing days required to complete the program—one for test at 3 days, one for test at 28 days, and one for test at 1 year. In the case

Table 2.—Concrete mix data ¹

Admixture			Series I: Limestone coarse aggregate				Series II: Gravel coarse aggregate				Series III: Limestone coarse aggregate			
No.	Physical state	Amount recommended	Admixture	Water	Air	Slump	Admixture	Water	Air	Slump	Admixture	Water	Air	Slump
BASE MIX: WITHOUT AIR-ENTRAINING ADMIXTURE														
None		Oz./sack	Oz./sack	Gal./sack	Pct.	In.	Oz./sack	Gal./sack	Pct.	In.	Oz./sack	Gal./sack	Pct.	In.
				5.6	1.0	3.1		5.0	1.0	3.0		6.1	1.5	2.6
GROUP A: SALTS OF WOOD RESINS														
1	Liquid	1-1½	1.00	5.2	5.1	3.3	1.02	4.6	4.2	3.0	1.00	5.6	6.0	2.7
2	do	1	.66	5.1	5.0	3.0					.67	5.6	6.6	3.0
3	do	½	.43	5.2	5.1	3.2					.48	5.6	6.8	3.0
4	do	½-1	.75	5.1	4.1	3.0	.92	4.7	4.4	3.1	.75	5.6	5.3	2.8
5	do	1.043	1.04	5.1	4.1	3.2					1.04	5.6	6.2	3.7
6	do	½-1	.59	5.1	3.7	3.2	.79	4.6	5.1	3.0	.63	5.4	4.8	2.7
7	Powder	.24	.12	5.1	5.1	3.6	.12	4.7	4.6	3.0	.13	5.6	7.7	3.5
GROUP B: SYNTHETIC DETERGENTS														
12	Flake	0.2-0.3	0.14	5.1	5.1	3.3	0.14	4.7	4.6	3.5	0.16	5.6	6.8	3.0
13	do	.08-.15	.08	5.1	5.1	3.5					.08	5.5	4.6	3.0
14	do	1	.16	5.1	5.2	3.0					.19	5.4	8.5	3.5
15	do		.06	5.1	5.2	3.0					.05	5.4	6.1	2.8
16	Liquid	1	.14	5.1	4.7	3.2	.19	4.6	4.9	3.6	.17	5.4	7.5	3.2
17	do		.14	5.1	4.9	3.0	.16	4.6	4.5	3.1	.13	5.4	6.3	3.4
26	do	½	.18	5.1	5.4	3.6	.19	4.6	4.4	3.1	.17	5.5	7.0	3.6
GROUP C: SALTS OF SULFONATED LIGNIN														
18	Powder	4.00	4.00	4.8	5.4	3.6					4.00	4.9	6.6	2.4
20	do	6.40	6.40	4.8	5.3	3.4					6.40	4.8	6.1	2.0
21	do	8.00	8.00	4.8	5.0	3.1					8.00	4.9	7.3	3.0
22	do	16.00	16.00	4.8	4.3	3.0					16.00	5.0	3.6	1.8
GROUP D: SALTS OF PETROLEUM ACIDS														
11	Liquid	¼-½	0.34	5.1	3.5	2.9	0.54	4.7	4.4	3.2	0.41	5.6	5.0	3.0
27	do	0.80	.80	5.1	3.9	3.2					.81	5.6	4.7	2.5
GROUP E: SALTS OF PROTEINACEOUS MATERIALS														
24	Liquid	¼-½	1.74	5.0	4.6	3.8	2.27	4.6	4.3	3.0	1.68	5.5	5.8	3.5
25	do	4	4.00	5.0	4.5	3.6	4.71	4.6	3.8	3.7	4.00	5.4	5.5	2.6
GROUP F: FATTY AND RESINOUS ACIDS AND THEIR SALTS														
8	Liquid	¾-1	0.75	5.2	3.9	2.9	1.37	4.7	4.5	3.5	0.76	5.6	3.5	2.4
9	do	½	.50	5.1	3.9	2.8	.67	4.7	4.5	3.4	.50	5.6	4.7	2.7
10	do	½-1	.58	5.1	3.8	2.9	1.03	4.6	4.0	3.5	.63	5.6	4.5	2.2
28	Semisolid		.37	5.0	4.5	3.2						5.6	7.7	3.6
GROUP G: ORGANIC SALTS OF SULFONATED HYDROCARBONS														
23	Liquid	¾-1	0.75	5.1	3.9	2.9	0.87	4.7	3.8	3.2	0.76	5.6	4.8	2.4

¹ See also table 2A. ² Percent by weight of cement.

Table 2A.—Proportions of concrete mixes by oven-dry weight, in pounds

Series	Coarse aggregate	Base mix			Air-entrained mix		
		Cement	Aggregate		Cement	Aggregate	
			Fine	Coarse		Fine	Coarse
I	Limestone	94	195	350	94	175	350
II	Gravel	94	170	370	94	153	370
III	Limestone	94	215	315	94	200	315

of all of the air-entrained concretes the values reported are, therefore, the averages of 3 tests made on different days, whereas the values reported for the base mix are the average of 10 tests made on different days.

A total of 4 mixing days was required to complete the specimens for Series II. For each of the 15 selected admixtures, three specimens of a kind were cast on each of 2 mixing days. From the concrete made the first day, two specimens of a kind were made for test at 28 days and one for test at 1 year. From the concrete made the second day, one specimen of a kind was cast for test at 28 days and two for test at 1 year. For the base mix, three specimens of a kind were made on each of the four mixing days. The specimens made during the first two days were tested at 28 days and those made the last two days at 1 year.

For each of the 27 admixtures and the base mix used in Series III, one 16 by 24 by 4-inch

slab was cast. Two mixing days were required for this portion of the program, one base mix slab being cast on each mixing day. After a preliminary curing period of 14 days in moist air followed by 35 days in laboratory air, each slab was prepared for test by sawing it into seven 3 by 4 by 16-inch beams.

All mixing was done in an open-pan type Lancaster mixer of 1¼ cubic-foot capacity. The following mixing cycle was employed: The cement plus the damp sand was first mixed for 30 seconds,

after which the estimated total quantity of mixing water plus the admixture, if any, was added and the mortar mixed for a further period of 1 minute. The coarse aggregate in a saturated, surface-dry condition was then added and the concrete mixed for an additional 2 minutes, making a total mixing period of 3½ minutes. Air contents were determined by the pressure method, A.S.T.M. test method C 231-49T. Consistency was controlled by means of the standard slump test.

Table 3.—Series I: Flexural and compressive strength of concrete with limestone coarse aggregate

Admix- ture	Air content ¹	Modulus of rupture ² at—						Compressive strength ³ at—					
		3 days		28 days		365 days		3 days		28 days		365 days	
		Strength	Ratio	Strength	Ratio	Strength	Ratio	Strength	Ratio	Strength	Ratio	Strength	Ratio
BASE MIX: WITHOUT AIR-ENTRAINING ADMIXTURE													
None	Pct. 1.0	P.s.i. 455	Pct. 100	P.s.i. 790	Pct. 100	P.s.i. 800	Pct. 100	P.s.i. 1,760	Pct. 100	P.s.i. 4,230	Pct. 100	P.s.i. 5,530	Pct. 100
GROUP A: SALTS OF WOOD RESINS													
1	5.1	430	97	730	92	730	91	1,750	99	3,950	93	4,980	90
2	5.0	420	94	770	97	810	101	1,540	87	3,910	92	5,110	92
3	5.1	455	102	710	90	710	89	1,680	95	3,950	93	5,030	91
4	4.1	400	90	745	94	790	99	1,730	98	3,880	92	5,390	97
5	4.1	455	102	775	98	800	100	1,810	103	4,130	98	5,590	101
6	3.7	475	107	820	104	810	101	2,110	120	4,390	104	6,070	110
7	5.1	420	94	730	92	740	92	1,660	94	3,950	93	5,100	92
GROUP B: SYNTHETIC DETERGENTS													
12	5.1	370	83	740	94	730	91	1,630	93	3,920	93	4,700	85
13	5.1	390	88	750	95	745	93	1,580	90	3,870	91	4,910	89
14	5.2	425	96	745	94	770	96	1,710	97	4,110	97	5,180	94
15	5.2	435	98	780	99	725	91	1,900	108	4,350	103	5,300	96
16	4.7	425	96	765	97	725	91	1,870	106	4,170	99	5,310	96
17	4.9	455	102	750	95	740	92	1,920	109	4,410	104	5,420	98
26	5.4	400	90	745	94	800	100	1,800	102	4,090	97	5,190	94
GROUP C: SALTS OF SULFONATED LIGNIN													
18	5.4	535	120	800	101	800	100	2,380	135	4,950	117	6,260	113
20	5.3	575	129	830	105	840	105	2,430	138	4,880	115	6,210	112
21	5.0	560	126	820	104	880	110	2,730	155	5,100	121	6,450	117
22	4.3	635	143	845	107	850	106	3,130	178	5,300	125	6,800	123
GROUP D: SALTS OF PETROLEUM ACIDS													
11	3.5	440	99	760	96	770	96	1,810	103	3,950	93	5,460	99
27	3.9	455	102	745	94	790	99	1,980	112	4,000	95	5,440	98
GROUP E: SALTS OF PROTEINACEOUS MATERIALS													
24	4.6	455	102	780	99	780	98	1,900	108	4,300	102	5,760	104
25	4.5	470	106	835	106	795	99	2,010	114	4,220	100	5,620	102
GROUP F: FATTY AND RESINOUS ACIDS AND THEIR SALTS													
8	3.9	440	99	770	97	770	96	1,830	104	4,130	98	5,180	94
9	3.9	480	108	840	106	815	102	1,870	106	4,450	105	5,070	92
10	3.8	510	115	855	108	870	109	2,070	118	4,330	102	6,000	108
28	4.5	465	102	770	97	760	95	1,930	110	4,370	103	5,530	100
GROUP G: ORGANIC SALTS OF SULFONATED HYDROCARBONS													
23	3.9	470	106	775	98	795	99	1,920	109	4,240	100	5,420	98

¹ Air content determined by A.S.T.M. tentative method C 231-49T.

² Specimens were 6 by 6 by 21-inch beams tested in accordance with A.S.T.M. standard method C 78-49. Each value for the base mix is the average of 10 tests and for all other groups is the average of 3 tests. Ratio values for relative strength are based on the strengths for the base mix.

³ Specimens were 6 by 12-inch cylinders tested in accordance with A.S.T.M. standard method C 39-49. Each value for the base mix is the average of 10 tests and for all other groups is the average of 3 tests. Ratio values for relative strength are based on the strengths for the base mix.

Testing Procedures

All strength specimens were molded, cured, and tested strictly in accordance with applicable A.S.T.M. procedures. All specimens were continuously moist cured until tested. Of the seven beams which were sawed from each slab cast in connection with the Series III program, two were subjected to freezing and thawing, two were tested for flexural strength at the start of the freezing test, and three were held for further tests. After sawing, the specimens for the freezing and thawing test and the corresponding control specimens were stored in laboratory air for 10 days and then immersed in water for 7 days prior to test. The specimens held for future tests were stored in moist air.

A 24-hour cycle was used in making the freezing and thawing tests. Specimens were frozen in water at -10° F. for 18 hours and thawed in water at 70° F. for 6 hours. Each specimen was frozen in an individual metal container of such size as to provide about one-eighth-inch clearance on all sides. The specimens in the containers were placed vertically in the freezing chamber. The refrigerant, in this case alcohol, entirely surrounded the containers to a height of about 18 inches. After each cycle, the specimens were removed from the containers and turned upside down. The water in the containers was also changed.

Resistance to the effects of alternate freezing and thawing was determined periodically during

the test by measuring changes in the dynamic modulus of elasticity of the concrete, with equipment of the type generally used for this purpose. Inasmuch as, for a given specimen, changes in dynamic E are proportional to changes in the square of the natural frequency of vibration (N^2) it is possible to use the reduction in N^2 directly as a measure of deterioration. This procedure avoids the necessity of calculating values for dynamic E and is the one customarily used. Freezing and thawing was continued until the specimens showed a loss in N^2 of approximately 40 percent, or for 200 cycles, whichever occurred first. They were then broken in flexure.

In order to express in a single figure the loss in N^2 as related to the number of cycles required

to produce that loss, a value known as the durability factor *DF* is used. The values for *DF* shown in table 5 were calculated as follows:

$$DF = (100 - L) \left(\frac{n}{200} \right)$$

Where:

DF = durability factor.

L = loss in *N*² at *n* cycles (from table 5).

n = number of the cycles at which the loss in *N*² reaches 40 percent, or 200 if loss in *N*² does not reach 40 percent by the end of the test (200 cycles).

The strength ratios reported in table 5 are the ratios of the flexural strengths of specimens after freezing and thawing expressed as percentages of the strengths of the corresponding control specimens, tested at the time the freezing and thawing test was started.

Discussion of Test Results

The results of these tests are shown in tables 2-5 and in figures 1-4. The data will be discussed in terms of the three principal objectives of the investigation. These were to determine, for each admixture, (1) its ability to entrain air in concrete, (2) its effect on the compressive and flexural strength of concrete, and (3) its effect on the durability of concrete.

Ability to Entrain Air

Table 2 shows, for each admixture and for each series, the amount of admixture to be used, as recommended by the manufacturer, the amount actually used, and the corresponding air and water content and slump of the concrete. It will be noted that, in most cases, the amount of admixture which was used was either the same as, or reasonably close to, the amount recommended. Principal exceptions were admixtures 14 and 16, where only about one-seventh of the recommended amount was used, and admixture 7, where only about half of the recommended quantity was used. The tendency, in general, was to use somewhat less than the amounts recommended.

In Series I and II (the strength tests) the amount of air entrained in the concrete was in every case within the usually specified limits of 3 to 6 percent. Actually the total range for the 27 admixtures was less than 2 percent (3.5 to 5.4 percent) with only 9 values out of 42 falling below 4.0 percent. The materials in group A, the salts of wood resins, in group B, the synthetic detergents, and in group C, the salts of sulfonated lignin, gave in general somewhat higher air contents than the materials in groups D, E, F, and G. This, of course, was on the basis of using an amount of admixture either the same as or close to the amount recommended. Increasing the quantity above the recommended amount would, of course, have raised the air content. However, as previously explained, adjustments of this sort were not made so long as the air content obtained with the recommended amount of admixture fell well within 3 to 6 percent.

As already noted, it was decided to use the same quantities of admixture in Series III (the durability tests) as were used in Series I, even though it was realized that, because of the higher

percentage of sand, higher air contents would probably be obtained. From table 2 it will be seen that the air contents in Series III were, in general, not only considerably higher than in Series I and II but that they were also more variable. The total range was from 3.5 to 8.5 percent, with 14 values above 6.0 percent, 5 values of 7.0 percent or more, and 2 values below 4.0 percent. Two possibilities occur as to the reasons for these comparatively wide variations. In the first place, each value in Series III was the result of only one test on one batch of concrete (the batch required for casting the 16 by 24 by 4-inch slab), whereas in Series I and II each value was the average of one test on each of three or two batches made on different days. In the second place, the higher sand mix used in Series III was probably somewhat more critical with respect to variables which affect air content than the low sand mixes used in Series I and II. However, as will be explained later, there appeared to be little or no relation between durability and total air content provided entrained air was present, so that from the standpoint of evaluating the individual admixtures these comparatively wide

variations in total air content were unimportant.

It may also be noted from table 2 that the consistency of the concrete was quite uniform throughout the tests. In Series I and II the maximum range in slump in 42 tests was only 1 inch, the maximum value being 3.8 inches and the minimum value 2.8 inches. In the case of Series III the range was somewhat greater, being 1.9 inches, with the maximum 3.7 inches and the minimum 1.8 inches. It is probable that these variations in slump accounted at least in part for the variations in air content obtained in Series III.

For each series the water contents of the various air-entrained concretes were about the same, with the exception of the four admixtures in group C, which required, on the average, about 0.4 gallon of water per sack less than the admixtures in the other groups. With this exception, the reduction in water content due to air entrainment was about 0.5 gallon per sack with a tendency towards a somewhat greater reduction in the case of Series III (high sand content, 1-inch maximum aggregate size) as compared to Series I (low sand content, 1½-inch maximum aggregate size).

Table 4.—Series II: Flexural and compressive strength of concrete with gravel coarse aggregate

Admix- ture	Air content ¹	Modulus of rupture ² at—				Compressive strength ³ at—			
		28 days		365 days		28 days		365 days	
		Strength	Ratio	Strength	Ratio	Strength	Ratio	Strength	Ratio
BASE MIX: WITHOUT AIR-ENTRAINING ADMIXTURE									
None	Pct. 1.0	P.s.i. 675	Pct. 100	P.s.i. 650	Pct. 100	P.s.i. 4,200	Pct. 100	P.s.i. 5,080	Pct. 100
GROUP A: SALTS OF WOOD RESINS									
1	4.2	695	103	610	94	4,050	96	4,760	94
4	4.4	690	102	620	95	3,880	92	4,860	96
6	5.1	700	104	600	92	3,670	87	4,990	98
7	4.6	635	94	575	88	3,910	93	4,750	94
GROUP B: SYNTHETIC DETERGENTS									
12	4.6	675	100	630	97	4,010	95	4,620	91
16	4.9	630	93	545	84	3,780	90	4,220	83
17	4.5	655	97	525	81	3,840	91	4,720	93
26	4.4	675	100	590	91	3,780	90	4,770	94
GROUP D: SALTS OF PETROLEUM ACIDS									
11	4.4	640	95	630	97	3,750	89	4,730	93
GROUP E: SALTS OF PROTEINACEOUS MATERIALS									
24	4.3	680	101	550	85	4,020	96	5,120	101
25	3.8	695	103	570	88	4,100	98	4,900	96
GROUP F: FATTY AND RESINOUS ACIDS AND THEIR SALTS									
8	4.5	680	101	575	88	3,760	90	4,570	90
9	4.5	695	103	575	88	3,770	90	4,660	92
10	4.0	720	107	630	97	3,650	87	5,010	99
GROUP G: ORGANIC SALTS OF SULFONATED HYDROCARBONS									
23	3.8	665	99	595	92	3,870	92	4,950	97

¹ Air content determined by A.S.T.M. tentative method C 231-49T.

² Specimens were 6 by 6 by 21-inch beams tested in accordance with A.S.T.M. standard method C 78-49. Each value for the base mix is the average of six tests and for all other groups is the average of three tests. Ratio values for relative strength are based on the strengths for the base mix.

³ Specimens were 6 by 12-inch cylinders tested in accordance with A.S.T.M. standard method C 39-49. Each value for the base mix is the average of six tests and for all other groups is the average of three tests. Ratio values for relative strength are based on the strengths for the base mix.

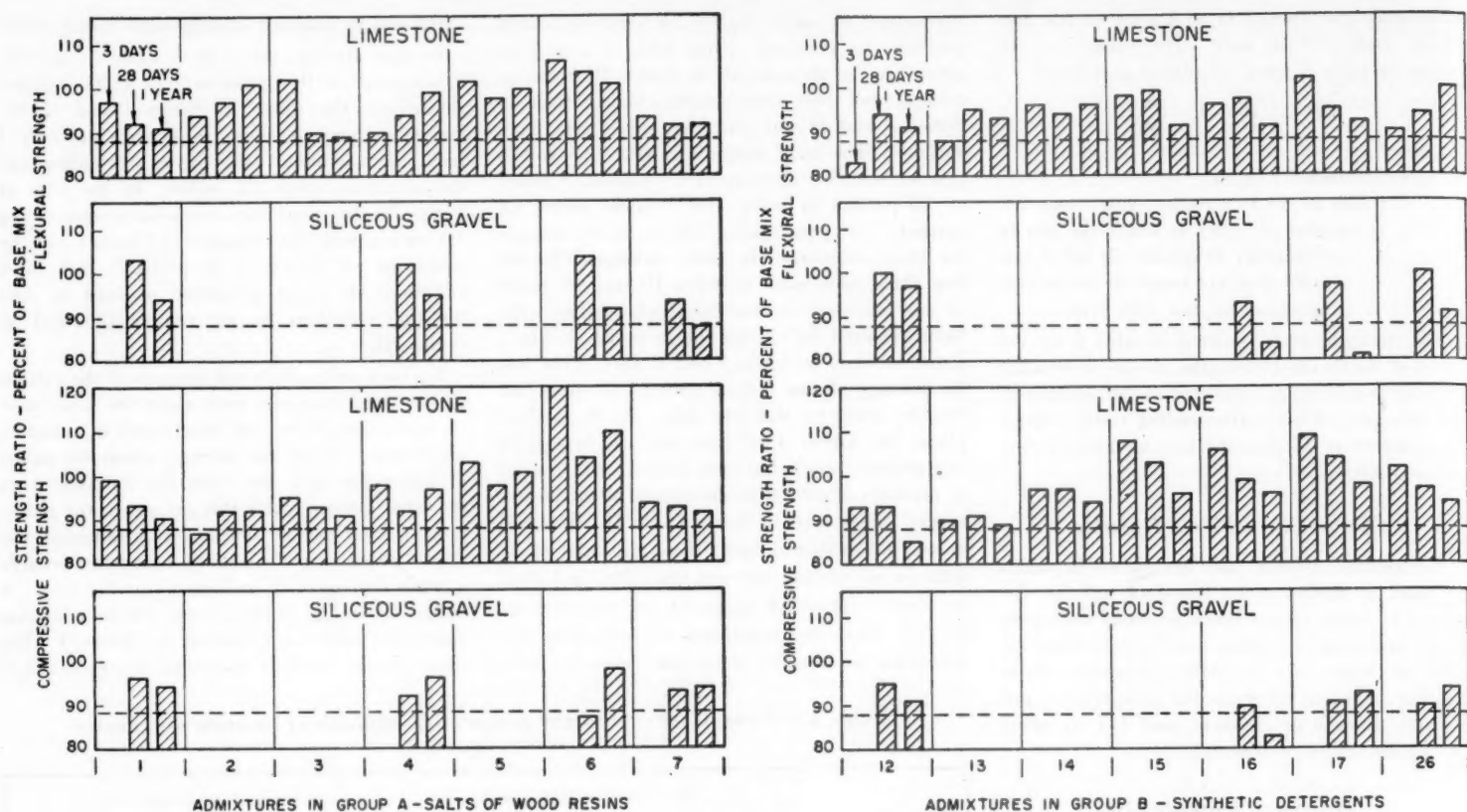


Figure 1.—Effect of air-entraining admixtures on strength of concrete: Groups A and B.

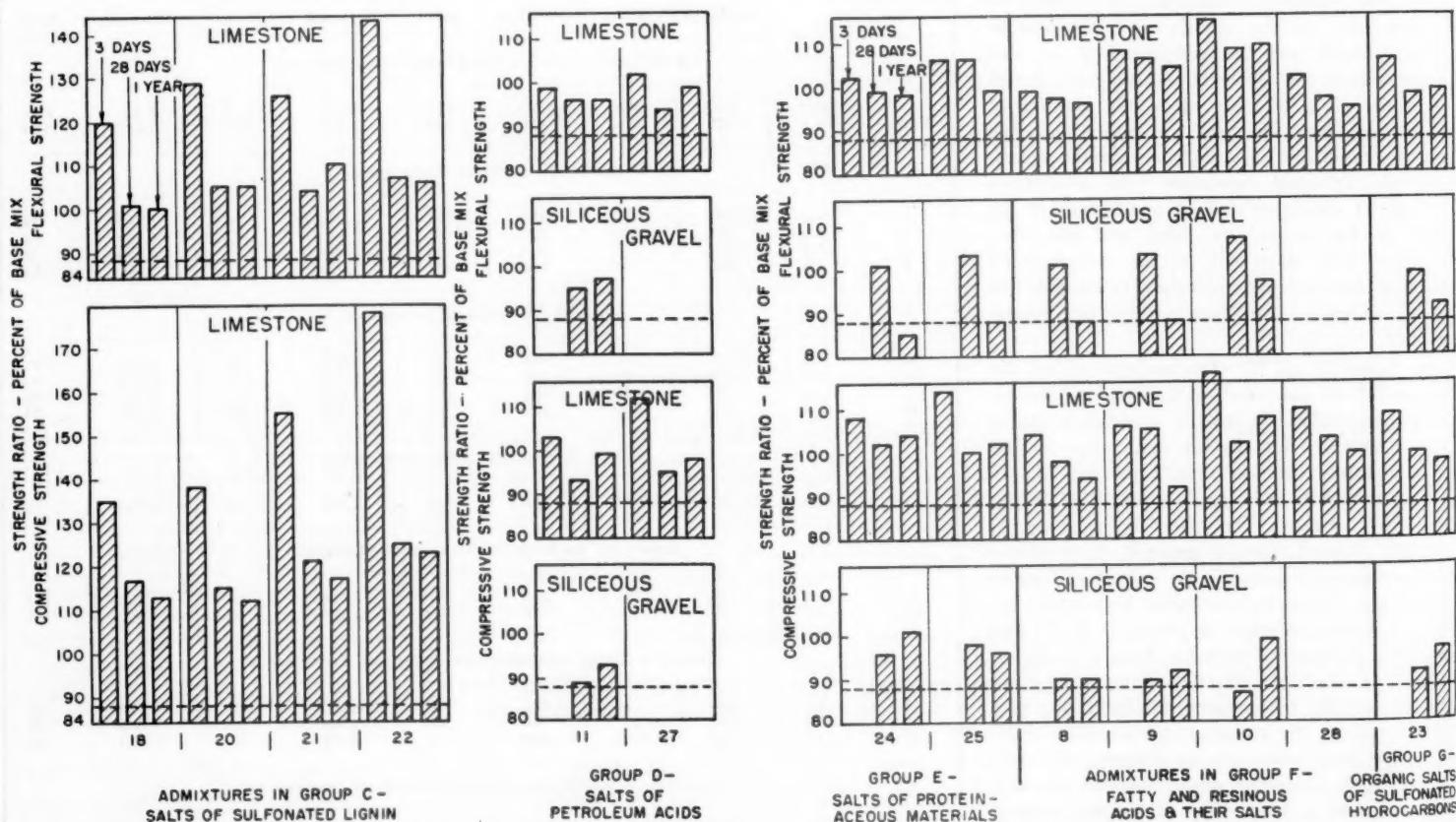


Figure 2.—Effect of air-entraining admixtures on strength of concrete: Groups C-G.

Effect on Strength

The flexural and compressive strengths of the crushed limestone concrete containing each of

the 27 admixtures and the base mix (Series I) are shown in table 3, with the corresponding data for the gravel concrete for 15 admixtures

only (Series II) in table 4. These tables also show, for each type of test and for each age tested, the ratios of the strengths developed with

the admixtures, expressed as percentages of the strengths of the corresponding concretes without admixture. The strength ratios for both series are also plotted graphically in figures 1 and 2. It will be convenient, in discussing the trends as shown by these graphs, to consider the seven groups of admixtures in order.

Group A

The strength ratios for the seven admixtures in group A (the salts of wood resins) are shown in the left half of figure 1. It is at once apparent that in practically all cases the strengths, both in flexure and compression, are at least 88 percent of the strengths of the corresponding base mix. In fact, out of a total of 58 values there are only 2 which are less than 88 percent—admixture 2, for which the compressive strength ratio of limestone concrete at 3 days was 87 percent, and admixture 6, for which the compressive strength ratio of gravel concrete at 28 days was 87 percent. It will be seen that failure to comply with the 88-percent requirement does not occur more than once with any admixture. On the basis of these data all seven of the materials in group A have been accepted as substantially meeting the requirement for strength.

There seems also to be a tendency for the flexural strength ratios to decrease with age. This tendency is quite definite in the case of the gravel concrete and appears in some degree in the limestone concrete in five out of the seven cases, although two of the admixtures, Nos. 2 and 4, show a distinct trend in the opposite direction. These trends are not so well defined in the case of compressive strength. Even here, however, there is a tendency for the relative strength of the limestone concrete to decrease with age.

In general, the strength level of the concretes containing the neutralized wood resin admixtures is about what would be expected with materials of this type in every case except for admixture 6. Although all of these materials were supposed to be salts of wood resins with nothing added, the comparatively high strengths (particularly at 3 days) developed by the concrete containing admixture 6 would indicate the possibility that an accelerator or activating agent of some sort was present in this case.

Group B

The corresponding strength ratios for the seven admixtures in group B (the synthetic detergents) are shown in the right half of figure 1. Again, most of the values are 88 percent or more of the base mix. In this group, however, we find several which are substantially below 88 percent, the lowest being 81 percent. In two cases (admixtures 12 and 16), two out of the ten values show ratios of less than 88 percent whereas, in the case of admixture 17, one out of ten values is less than 88 percent.

As in group A, there is a tendency in group B for the strength ratios to decrease with age. Of the 22 comparisons in the right half of figure 1, 17 show this tendency in some degree. A definite reversal is indicated in only three instances. These are admixture 26, limestone concrete in flexure and gravel concrete in compression, and admixture 17, gravel concrete in compression. On the

basis of the data, all seven of the admixtures in group B have been accepted as substantially meeting the requirement for strength.

Group C

The strength ratios developed by the crushed limestone concrete containing the four admixtures in group C (salts of sulfonated lignin) are shown in the left side of figure 2. All of these materials (the products of one manufacturer) developed substantially higher strengths, particularly at 3 days, than any of the other admixtures. In the case of three of the four admixtures in this group, Nos. 20, 21, and 22, high early strength was probably due, at least in part, to the presence of substantial amounts of calcium chloride in the admixture. In fact, there seems to be a fairly good relation between the amount of calcium chloride in the admixtures, as revealed by chemical analysis, and the 3-day strength. However,

the fact that strength ratios as high as 135 in compression and 120 in flexure at 3 days were developed by admixture 18 which, according to the manufacturer's statement, contained no calcium chloride, would indicate that some other factor, possibly the dispersing effect of the calcium lignosulfonate on the cement, contributed to the high strengths which were obtained. It is also interesting to note that, in the case of all four of the group C materials, concrete of the required consistency was obtained with water contents approximately 0.3 to 0.4 gallon per sack of cement less than was required for the other materials (see table 2).

Group D

Strength ratios for the two materials in group D (salts of petroleum acids) are shown in the center of figure 2. All of the values are above the 88-percent limit set for evaluation purposes. How-

Table 5.—Series III: Summary of freezing and thawing tests

Admix- ture	Air content	Loss in N ^o at—cycles						Cycles at 40 percent loss	Dura- bility factor	Modulus of rupture		
		10	50	100	150	180	200			Control spec- imen	Frozen and thawed specimen 1	Str'gth ratio
BASE MIX: WITHOUT AIR-ENTRAINING ADMIXTURE												
None	Pct. 1.5	Pct. 16	Pct. 254	Pct. -----	Pct. -----	Pct. -----	Pct. -----	27	8	P.s.i. 890	P.s.i. 280 (32)	Pct. 31
GROUP A: SALTS OF WOOD RESINS												
1	6.0	4	8	24	35	40	-----	180	54	770	375 (180)	49
2	6.6	5	8	22	34	39	-----	182	55	715	355 (180)	50
3	6.8	5	8	24	34	41	-----	178	53	690	360 (180)	52
4	5.3	5	9	28	39	52	-----	155	46	860	360 (180)	42
5	6.2	4	7	17	28	34	341	3195	359	800	-----	-----
6	4.8	2	3	15	24	28	34	200+	66	840	420 (200)	50
7	7.7	4	6	21	35	42	-----	174	52	725	360 (180)	50
GROUP B: SYNTHETIC DETERGENTS												
12	6.8	3	7	21	34	41	-----	178	53	690	360 (180)	52
13	4.6	5	6	20	30	33	37	200+	63	770	455 (200)	59
14	8.5	5	6	21	32	38	-----	186	56	800	400 (180)	50
15	6.1	5	7	17	27	29	35	200+	65	735	425 (200)	59
16	7.5	2	5	17	26	30	36	200+	64	795	390 (200)	49
17	6.3	5	6	18	28	33	40	200	60	780	440 (200)	56
26	7.0	5	6	18	28	32	39	200+	61	800	345 (200)	43
GROUP C: SALTS OF SULFONATED LIGNIN												
18	6.6	4	5	14	22	26	31	200+	69	970	445 (200)	46
20	6.1	4	8	17	25	28	34	200+	66	920	495 (200)	54
21	7.3	2	6	17	26	29	35	200+	65	950	385 (200)	41
22	3.6	2	11	24	37	44	-----	163	49	1000	490 (180)	49
GROUP D: SALTS OF PETROLEUM ACIDS												
11	5.0	5	7	22	36	49	-----	159	48	915	340 (180)	37
27	4.7	5	10	26	38	48	-----	156	47	780	305 (180)	42
GROUP E: SALTS OF PROTEINACEOUS ACIDS												
24	5.8	3	7	22	32	37	44	189	57	860	410 (200)	48
25	5.5	2	7	18	32	40	-----	180	54	935	425 (180)	45
GROUP F: FATTY AND RESINOUS ACIDS AND THEIR SALTS												
8	3.5	8	22	46	-----	-----	-----	80	24	790	280 (85)	35
9	4.7	4	11	33	543	-----	-----	118	35	780	380 (125)	49
10	4.5	3	5	21	28	36	55	185	56	920	320 (200)	35
28	7.7	6	7	23	31	34	39	200+	61	650	370 (200)	57
GROUP G: ORGANIC SALTS OF SULFONATED HYDROCARBONS												
23	4.8	5	13	28	39	46	-----	152	46	760	350 (180)	46

Each value is the average of two tests.

1 Figures in parentheses indicate number of cycles at which test was made.

2 Tested at 32 cycles.

4 Tested at 85 cycles.

3 Specimens damaged after 180 cycles. Value estimated from probable curve.

5 Tested at 125 cycles.

ever, there is the same tendency for the ratios to decrease with age as has been previously noted, except that in the case of these materials a general tendency to recover strength somewhat between 28 days and 1 year is also noted. These two admixtures therefore met the requirement for strength.

Groups E, F, and G

Strength ratios for the materials in group E (salts of proteinaceous materials), group F (fatty and resinous acids and their salts), and group G (organic salts of sulfonated hydrocarbons) are shown in the right side of figure 2. It will be noted that, in the case of the limestone concrete, all of these materials meet the 88-percent strength requirement, both in flexure and compression. In the case of the gravel concrete in flexure, however, one of the materials (No. 24) is below the 88-percent limit at 1 year, while in compression one material (No. 10) is slightly under at 28 days. Again, the tendency for the strength ratios to decrease with age is apparent, although the differences in some instances are not significant. These materials have all been accepted as complying substantially with the requirement for strength.

Effect on Durability

The data from the freezing and thawing tests are shown in tabular form in table 5. The results are presented as the loss in N^2 at 10, 50, 100, 150, 180, and 200 cycles, the number of cycles required to cause a 40-percent reduction in N^2 , the durability factor, the modulus of rupture determined both at the conclusion of the freezing and thawing test and on the corresponding control specimens, and the ratio of the flexural strength of the frozen and thawed specimen expressed as a percentage of the strength of the corresponding control specimen. The reductions in N^2 plotted against the number of cycles of freezing and thawing are shown for each admixture in figure 3, while in figure 4 the durability factors and the corresponding ratios of the strengths of the frozen and thawed specimens to the strengths of the control specimens have been plotted in bar diagram form.

In view of the fact that the durability factor is generally considered to be a satisfactory measure of the effect of alternate freezing and thawing, this value will be used as the primary basis of comparison of the various admixtures. This will be followed by a brief discussion of the value of the strength test for the same purpose.

Durability Factor Comparisons

For the seven materials in group A (salts of wood resins), it will be noted that the durability factors range from a low of 46 to a high of 66, as compared with 8 for the base mix without air entrainment. Air contents varied from 4.8 to 7.7 percent. However, there appears to be little or no relation between total air content and durability. For example, the admixture with the lowest air content, No. 6, shows the highest durability factor, 66, whereas the admixture with the highest air content, No. 7, has next to the lowest durability factor. These apparent discrepancies may be related to a variable which,

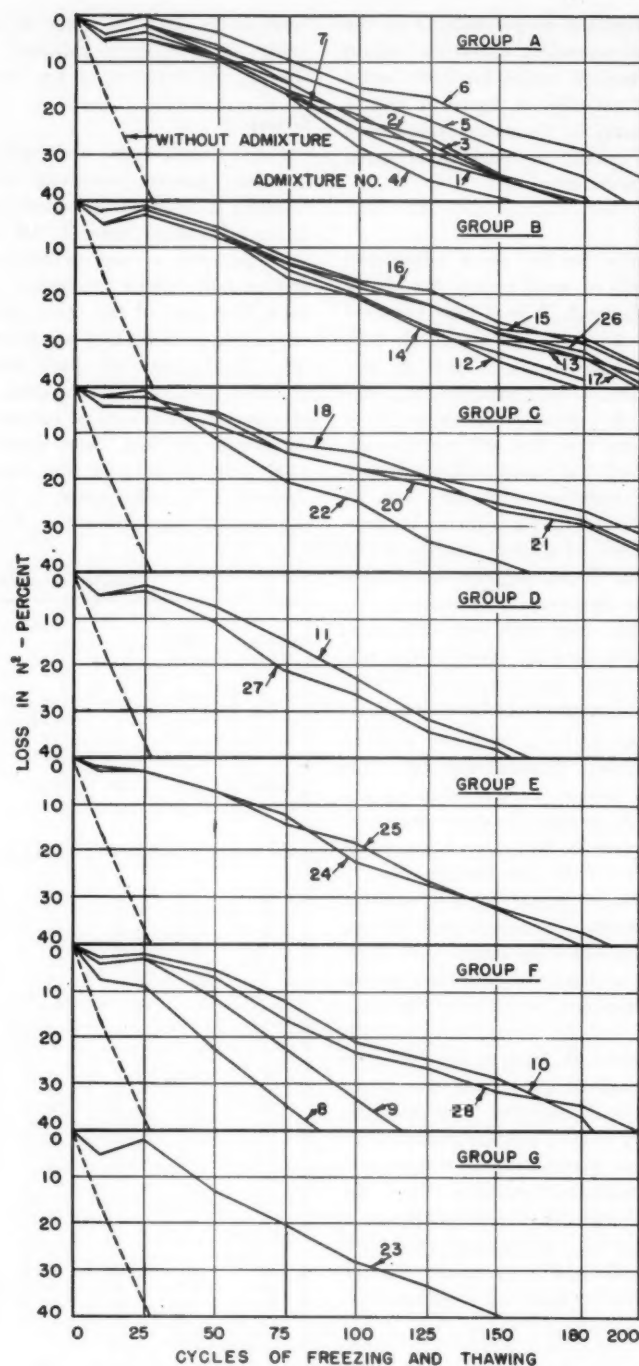


Figure 3.—Resistance of concrete to alternate freezing and thawing as influenced by different air-entraining admixtures.

although not as yet clearly understood, is being intensively studied—the effect on durability of size and distribution of the air voids in the concrete. This is a variable which, so far, has been impossible to control in the laboratory. There is good reason to believe that variations in the size and spacing of the bubbles of entrained air in concrete may well cause marked differences in durability even though the total air content remains the same, and it is quite possible that uncontrolled variations of this kind may account for the lack of correlation between total air content and durability factor shown by these tests.

In group B (the synthetic detergents), the

durability factors vary from a low of 53 to a high of 65. Five of the seven values are 60 or more, indicating a considerably higher general level for this group than for group A. Air contents vary from 4.6 to 8.5. As in group A, however, there is little correlation between total air content and durability, indicating in this case also the influence of some uncontrolled factor.

The materials in group C (salts of sulfonated lignin), with the single exception of admixture 22, attained a higher general level of durability than those of any of the other groups. In this case there does seem to be some relation between air content and durability, at least so far as admixture 22 is concerned. This particular mem-

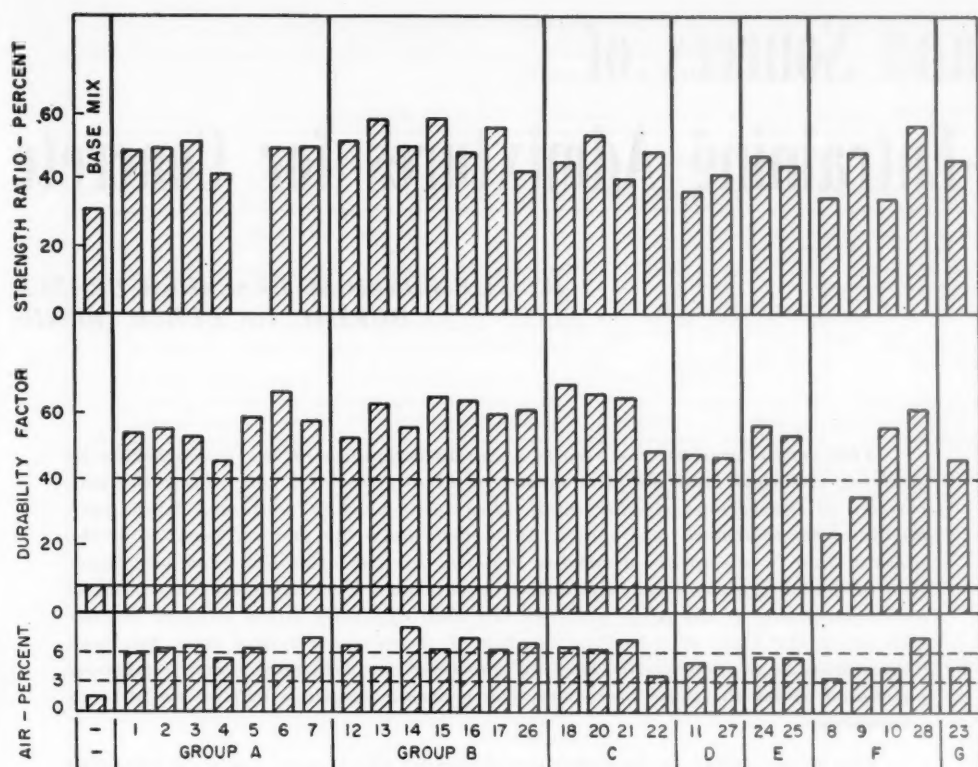


Figure 4.—Results of freezing and thawing tests.

ber of the group had an air content of 3.6 percent, the lowest of the group by a wide margin. It also showed the lowest durability factor of any of the four materials in this group. Although it may be without significance, it is interesting to note that a chemical analysis of admixture 18, having the highest durability factor in the group, revealed the presence of only a trace of calcium chloride. All of the other materials in the group contained an appreciable quantity of this salt.

The durability factors of the two materials in group D (salts of petroleum acids) were somewhat lower than the general level for groups A, B, and C. Durability factors of two of the materials in group F (fatty and resinous acids and their salts)—admixtures 8 and 9—were also comparatively low. The other two materials in

group F, as well as the two admixtures in group E (salts of proteinaceous materials), showed durability factors at about the same general level as the first two groups but somewhat lower than group C. As in other instances, the durability factors of the materials in these groups bear little relation to total air content except possibly for admixture 8. The concrete containing this admixture, with air content of only 3.5 percent, showed the least durability factor of any of the materials tested.

The one admixture classified in group G (organic salts of sulfonated hydrocarbons) produced concrete with a durability factor of 46, somewhat below the general level of groups A, B, and C. This concrete contained 4.8 percent air.

NEW PUBLICATIONS

Now available is the *Annual Report of the Bureau of Public Roads, Fiscal Year 1953*, which may be purchased from the Superintendent of Documents, Government Printing Office, Washington 25, D. C., at 25 cents a copy. The 45 pages of text and 27 pages of statistical tables describe the operation of the Federal-aid highway program during the fiscal year ended June 30, 1953. Also

reported are the Bureau's construction, research, and foreign activities during the period.

Also available is the Bureau's *Highway Statistics, 1952*, the eighth of the bulletin series presenting annual statistical and analytical tables of general interest on the subjects of motor fuel,

Flexural Strength Loss

The last column of table 5 shows the relative effect of freezing and thawing on flexural strength. In making comparisons between admixtures on the basis of strength loss, the number of cycles at which the test was made must be taken into consideration. For example, the strength ratio of 31 shown for the base mix cannot be compared directly with the corresponding ratios for any of the air-entrained concretes because the base concrete was tested after only 32 cycles whereas for most of the admixtures the strength tests were made after either 180 or 200 cycles. It was to take care of this variable that the durability factor was developed. For any given number of cycles, however, the strength ratios can be compared directly. For example, in the case of the 12 concretes which were tested for strength at 180 cycles, the two methods with one exception correlate reasonably well. Except for this case (admixture 11), the range in durability factor was from 46 to 55, with the corresponding range in strength ratio from 42 to 52.

Summary of Durability Tests

Summarizing, it has been shown that all of the admixtures included in this program, when used in amounts sufficient to entrain 3 to 6 percent air, substantially improved the durability of concrete. There was, however, a considerable range in the relative resistance of the various air-entrained concretes, the durability factors varying from a low of 24 for admixture 8 to a high of 69 for admixture 18. It has been shown that these variations are not related to the total air content of the concrete but that they may very well be due to some as yet uncontrolled variable related to air content, such as the size and spacing of the air bubbles. On the basis of these tests it is concluded that all of the admixtures included in this study, except No. 28 which, as has been stated, was submitted in such form as to require further processing before use, should be classified as satisfactory provided they are used in quantities which will entrain between 3 and 6 percent air in the concrete. A list of the acceptable admixtures appears on page 278.

Chemical Analysis and Sources of Air-Entraining Admixtures for Concrete

BY THE PHYSICAL RESEARCH BRANCH
BUREAU OF PUBLIC ROADS

Reported by WOODROW J. HALSTEAD
and BERNARD CHAIKEN, Chemists

THE CHANGES in properties caused by entrained air in portland cement concrete have been studied extensively and information is generally available to show the immediate effects to be expected for a given amount of entrained air. Since most of this work has been done with only three approved admixtures, each of which is a proprietary product, the longtime effects of these particular materials on the strength and durability of the concrete are also well established. Recently, however, the number of air-entraining admixtures on the market has increased greatly and, while their ability to entrain air in the concrete and their initial effect on its strength can be determined within a relatively short time, the demonstration of their effect on longtime strength as well as on durability requires much more extensive testing.¹

The American Society for Testing Materials has adopted a tentative specification for air-entraining admixtures, C 260-52T, and a method of test, C 233-52T (1).² In effect, this specification and method of testing describe a lengthy program of evaluation of the admixture by comparing most of the important properties of concrete specimens made both with and without the admixture. Because of the length of time and expense involved in such a program, however, it is impracticable to apply as a control measure. Accordingly, once a product has been shown to be satisfactory, the general policy of many consumer organizations is either to approve subsequent use of the material without further tests or to require only tests to determine ability to entrain air and effect on strength.

Unfortunately, even when the latter practice is followed there is no assurance that materials supplied at different times under the same brand name will be uniform in composition, since the results of limited performance tests will not necessarily reflect changes in the composition of a product. Appreciable alteration in the composition of a product could affect its influence on the strength and durability of the concrete and thus it is extremely desirable to obtain some assurance that each lot of material will have substantially the same composition as that initially approved.

¹ A companion article in this issue presents an evaluation of the same air-entraining admixtures that are considered here. The samples are identically numbered in both cases. In this article the samples are grouped according to treatment for chemical analysis, but in the evaluation study they are grouped according to source.

² Italic numbers in parentheses refer to the list of references in appendix III, p. 277.

This article presents the results of an investigation of the practicability of applying chemical analyses as a means of identifying and controlling the uniformity of the various air-entraining admixtures used in concrete. Some such means of identification and control is needed, since the general practice at the present time is to approve a specific material for use after extended laboratory tests or actual experimental installations have shown it to be satisfactory. Subsequent purchases of the same material are then approved either without further tests or on the basis of a limited number of short-term physical tests, but such limited tests do not necessarily give the consumer any assurance that the material purchased under the same trade name on separate occasions will be uniform in composition.

This investigation showed that air-entraining admixtures could be classified into a limited number of types, each of which contained major constituents that could be fairly easily determined in the laboratory. It is concluded that the quantitative determinations of these constituents can be used as means for adequately ascertaining the uniformity of different lots of the same materials, something which cannot be accomplished by short-term physical tests as now applied.

A qualitative scheme for the classification of unknown materials as to the type or types of compounds present was developed as a part of this investigation. The principles applied in making the quantitative determinations of the various constituents are discussed and the methods that are suitable for use in each case are given.

Chemical Analysis Approach

Some scheme of chemical analysis would appear to be the most direct approach to this end, but the complex chemical nature of the admixtures on the market has generally discouraged the development of laboratory methods for the analyses of most of these materials. It has been generally considered that such tests would be too involved and time consuming for practical applications. However, a study of the literature and the results of chemical analyses of a wide variety of commercial admixtures have shown that, despite the complexity of these materials, they are derived from a limited number of sources and can be chemically differentiated into a few basic types. It was also found that relatively simple tests are available to the analyst for qualitatively identifying the type and for quantitatively determining one or more of the chief constituents of each type. Thus, while chemical tests alone cannot be used as an indication of the ultimate behavior of an admixture in concrete, they can be used to give the consumer some assurance of the uniformity of different lots once a material has been proved satisfactory.

This article presents a scheme of identification and methods of analysis which are applicable to various types of admixtures. Also included is a

discussion of the sources of these various types. The data presented are based on the results of chemical analyses made on 28 samples of commercially marketed materials from 19 different manufacturers. At the time they were obtained, these materials were considered to be representative of all the various types on the market. New materials which have appeared since these were first obtained may not necessarily be of the same types but it is believed that, even where new types have been introduced, somewhat the same general procedures will be applicable with slight modifications and additions of definite identification tests.

Sources of Admixtures

The primary action of any concrete admixture used chiefly for air entrainment is that of a foaming agent. Thus, they are surface-active agents and as such are closely allied to the products of the detergent and emulsifier industries. Many of the materials marketed as concrete admixtures are obtained as byproducts of various industries or have been developed from materials which were originally classified as waste. The materials tested were found to originate from five major sources: petroleum refining processes, paper pulp manufacture, wood stump processing (in the

Table 1.—Qualitative identification of main constituents in air-entraining admixtures

Add water to original material; shake; note solubility.											
If completely soluble, see part A. If emulsion forms, see part B. If an insoluble phase or deposit forms, see part C.											
A. Completely soluble:											
Acidify water solution with hydrochloric acid. Note presence of separation.											
Fatty layer separates:				No definite separation: Make Biuret test (test 5) on original material.							
Test water solution of original material for ammoniacal nitrogen (test 2) and albuminoid nitrogen (test 1).				Positive result:		Negative result: Test ash of original material for sulfate.					Sulfate absent: Such material not included in this study.
Test ash of original material for cations (sodium, potassium, and calcium) and anions (sulfate, chloride, and carbonate).				Indicates proteinaceous acids or salts.		Sulfate present:					
Extract the fatty layer with chloroform and dry. Saponify a portion with alcoholic potassium hydroxide, evaporate, dry, and ignite. Test this ash for sulfate.				Ignite original material.		Indicates sulfonated lignin salts, sulfonated alkyl aryl salts, or inorganic sulfate.					
Test original material with permanganate (test 7).				Ash prominent:		Ash negligible:		Color not discharged immediately:			Color discharged immediately: Indicates sulfonated lignin salts. Test aqueous solution of original material for anions and cations.
Indicates proteinaceous salts of metals.				Indicates proteinaceous acids.		Indicates alkyl aryl sulfonate salt and/or inorganic sulfates.					
Test for anions and cations (especially calcium).				Determine solubility in 95-percent alcohol.							
Sulfate present:				Completely soluble:		Completely insoluble:		Partially soluble:			
Indicates a salt of a sulfonated hydrocarbon.				Indicates alkyl aryl sulfonate without builder.		Indicates inorganic sulfates.		Indicates alkyl aryl sulfonates with builder.			
Sulfate absent: Indicates a soap.				Indicates rosin or pine wood resin soap.		Indicates naphthenic or fatty acid soap.		Indicates fatty acid soap.		Indicates naphthenic acid soap.	
Make Liebermann-Storch test (test 6) on portion of chloroform extract.				Positive result:		Negative result:		Determine solubility of the chloroform extract in ligroine (petroleum ether) or gasoline. ¹			
Substantially soluble:				Substantially insoluble:		Easily soluble:		Difficult to dissolve or insoluble:			
Indicates rosin soap.				Indicates resin soap.		Indicates fatty acid soap.		Indicates naphthenic acid soap.			
B. Emulsion forms:											
To the original material add sufficient alcohol and water to obtain a 50-percent alcohol-water solution. Extract with ligroine or ethyl ether.				C. Insoluble phase or deposit:							
With the alcohol-water phase, remove the solvent by evaporation.				Insoluble matter still evident:				Completely soluble:			
A substantial amount of extract indicates soaps or sulfonated hydrocarbon salts.				Make Biuret test (test 5) on original material.				Indicates presence of soap-forming acids and/or unsaponifiable matter.			
Examine by procedures for completely soluble material in part A.				Positive result: Indicates glue.				Negative result:			
With the ligroine or ether phase, evaporate the solvent. Add an aqueous solution of sodium hydroxide; shake. (Heat to saponify if necessary.)				Run molybdate test (test 4) or tannic acid test (test 3) on original material.				Such material not included in this study.			
Completely miscible:				Positive test:				Negative test:			
Indicates presence of unsaponified organic acids in original material.				Substantiates presence of glue.				Such material not included in this study.			
Partially miscible:				Determine solubility of dried original material in 95-percent alcohol (cold).				Material in water-alcohol solution indicates original presence of soap-forming acids.			
Indicates presence of both free acid and unsaponifiable matter in original material.				Partially soluble:				Material in ligroine solution indicates unsaponifiable matter.			
Completely immiscible:				Indicates other organic material also present.				For further identification, test according to procedure in part A.			
				Test ash of alcohol-soluble matter for sulfate. ²				Further tests should be quantitative.			

tion so that the type or types of compounds present in their product can be surmised without qualitative tests, but often a material is received in the laboratory for which such information is not known. In such cases, qualitative tests must be conducted. There are several qualitative and quantitative methods of examination that cover a wide variety of wetting, dispersing, and emulsifying agents which may be used to advantage (10, 11, 12). In all cases, however, they do not adequately cover the present field of commercial admixtures.

Table 1 presents a scheme of identification which is believed to be adequate for all the types of materials examined in this investigation. This scheme was evolved from the actual results of the qualitative tests made, and is based on the consideration of the presence of only one major type of material except where combinations are normally expected. The presence of one type of material does not necessarily imply the absence of any other. Thus, for complete information where positive indications are obtained, tests under the negative indications must also be run. For mixtures of two or more types, some of the tests listed will be inconclusive. Despite these shortcomings, however, this systematic approach to the classification of unknown materials will save much time and give the required information for most of the commercial admixtures on the market at the present time.

Details of the various tests indicated by number in table 1 and also in the subsequent discussions are given in appendix II (p. 276).

Analysis of Soaps

The analytical procedures presented for the soap group are applicable to fatty, rosin, resin, and naphthenic acid soaps of alkalies, ammonia, or amines. Unsaponified matter may or may not be present. Of these materials, the rosin and fatty acid soaps are usually referred to as "true soaps," whereas the others are often designated as salts of the particular type of carboxylic acid concerned.

Eleven of the admixtures examined are in this group and the results of the tests on these materials are shown in table 2. Samples 1-6 are aqueous solutions of sodium soaps of resins extracted from wood. Sample 7 contains the same type material as samples 1-6 but was marketed as the dried product. Sample 8 is an aqueous solution of sodium soaps of fatty acids, resin (lignin) acids, and perhaps some rosin acids. Sample 9 is an aqueous solution of triethanolamine and sodium soaps of rosin, resin (lignin), and perhaps some fatty acids. Sample 10 is an aqueous solution of ammonium and sodium soaps of rosin and resin (lignin) acids containing appreciable unsaponified matter; it probably also contains some fatty acid soaps. Sample 11 is

an aqueous solution of sodium soaps of carboxylic acids (most likely naphthenic). Samples 1-7 were derived from processing pine wood stumps, samples 8-10 are probably byproducts of the paper pulp industry, and sample 11 is evidently derived from petroleum refining processes.

As indicated in table 1, all of these materials and materials of the same general type are characterized by fair solubility in water and incompatibility in dilute hydrochloric acid, the organic acids separating out of solution under such conditions.

Quantitative determinations

The quantitative determinations which are considered necessary for the basic evaluation of materials in this group are those of moisture content (tests 24 or 25), ash (test 12), and total fatty matter (test 18). The determination of moisture by the oven-drying method gives a fairly reliable measure of the concentration of inorganic and organic constituents in aqueous solutions. When analyzing petroleum products such as naphthenic soaps, however, there is some danger of volatilizing some petroleum constituents. In these cases a direct water-content determination by the distillation method is recommended. This procedure involves an azeotropic distillation using some fairly low-boiling solvent such as toluene or xylene. The ash determination represents a measure of inorganic metals or metal salts present and the

Table 2.—Analyses of soap materials

Identification Number											
	1	2	3	4	5	6	7	8	9	10	11
CHARACTERISTICS											
Probable source	Pine wood stumps						Paper pulp byproducts			Petroleum refining	
Form	Liquid						Solid	Liquid			
Color	Very dark brown						Brown	Dark brown Rosin	Brown Ammonia	Dark brown Petroleum	
Odor	Pine oil						Wood pulp				
QUALITATIVE TESTS											
Solubility:											
In water	Soluble							Turbid		Soluble	
In aqueous sodium hydroxide								Soluble			
In dilute hydrochloric acid	Fatty layer separates										
Ash:											
Presence	Present										
Anions present	Carbonate ¹										
Cations present	Sodium ²										
Extracted acids:											
Liebermann-Storch test for rosin	Positive							Not determined		Negative Insoluble	
Solubility in ligroine	Essentially insoluble									Trace	
Ammoniacal nitrogen	Not determined							Negative		Positive	
Albuminoid nitrogen	Not determined							Positive		Negative	
QUANTITATIVE DETERMINATIONS											
Solids percent	15.3	11.3	27.6	16.2	14.9	15.6	96.9	12.9	12.4	17.9	15.2
Ash do								2.0	.8	1.1	2.2
Sodium hydroxide do	1.9	1.3	3.3	2.1	2.0	1.4	8.6				
Triethanolamine do									2.1		
Total nitrogen do									.4		
Ammoniacal nitrogen do										.8	
Fatty matter:											
Total do	10.1	10.0	22.6	12.5	11.5	14.2	74.9	10.9	5.3	16.8	14.1
Rosin ³ do									86.8	31.2	
Methoxyl ⁴ do	4.9	2.1	4.2	4.6	5.3	4.4	3.2	.5	4.0	.3	
Unsaponified matter ⁵ do										36.3	

¹ Sample 8 also contains sulfate.

² Sample 6 also contains potassium.

³ Probably low because of volatility of petroleum constituents.

⁴ Sample 6 also contains potassium hydroxide.

⁵ Probably low because of emulsions formed during extraction.

⁶ Results expressed as percentages of total fatty matter.

⁷ Determination made on original material: the calculated percentage is therefore probably high since the total fatty matter was low.

ash should be qualitatively analyzed for the alkali and alkaline earth metals—sodium, potassium, and calcium. The anionic groups—sulfate, chloride, and carbonate—should also be determined. The term total fatty matter, as applied here, represents all the organic matter extracted by chloroform from an acidified aqueous solution of the admixture. It includes all the unsaponified and unsaponifiable constituents originally present in the material as well as the organic acids resulting from the breakdown of the soaps.

Other Tests

In order to obtain further information as to the type of soap present, additional determinations must be made, the necessary tests being dictated by the nature of the soap or soaps. At times, the odor of the material may be used as a clue to the presence of certain constituents. A strong odor of petroleum indicates a naphthenic acid soap while a pulp-like smell suggests a soap derived from paper pulp wastes. Where a fair amount of rosin soap is present, the characteristic odor of rosin usually will be evident.

As shown in table 1 (part A) when rosin is indicated to be present by the Liebermann-Storch test (test 6), further confirmation is needed inasmuch as soaps of lignin resins derived from pine wood also give a positive indication of rosin because of incomplete separation during the extraction processes. In these cases the solubility of the extracted total fatty matter in ligroine (petroleum ether) should be evaluated. Where substantial solubility exists, rosin soaps in appreciable amounts are indicated and they should be determined by the standard A.S.T.M. (Mc-Nicoll) method (test 29). If the material is essentially insoluble in ligroine and a positive Liebermann-Storch test has been obtained, a lignin-derived resin soap (pine wood extracts) is indicated. The lignin or total resin, as such, is difficult or impossible to determine directly. However, lignin is characterized by certain methoxyl groupings ($-OCH_3$) in its structure and although the amount of methoxyl is dependent upon the type of wood, the source, and method of processing, it is generally considered to be nearly constant for resins from the same source and process. Thus, a determination of this constituent (test 23) is a means of comparing materials from the same source. Where the average methoxyl content of the resins is known, the approximate percentage of the latter constituent may be calculated.

When the extracted total fatty matter gives a negative test for rosin and is essentially insoluble (or very slowly soluble) in ligroine, naphthenic acids are indicated. The quantitative procedure presented for these materials is based on the formation of their copper salts and their solubility in benzene (test 26). A negative test for rosin coupled with a high degree of solubility in ligroine is indicative of fatty acids or unsaponifiable matter. If unsaponified or unsaponifiable matter is believed to be present in the original material, they should be determined by extraction from a 50-percent alcohol-water solution with ligroine or ethyl ether (test 36). This is a measure of any free organic acids and unsaponifiable oils, fats, etc., which may be present. Fatty acid soaps are indicated by difference after determining the other constituents. They may be characterized by

Table 3.—Analyses of alkyl aryl sulfonate detergents

	Identification number					
	12	13	14	15	16	17
CHARACTERISTICS						
Probable source	Synthesized from petroleum distillates					
Form	Solid			Liquid		
Color	Cream			Pale yellow		
Odor	Petroleum					
QUALITATIVE TESTS						
Solubility in water	Soluble					
Aqueous solution:						
Compatibility with dilute hydrochloric acid	Compatible					
Permanganate test	Does not decolorize rapidly					
Alcohol-soluble material:						
Anions in ash	Sulfate					
Cations in ash	Sodium					
Alcohol-insoluble material:						
Presence	Present			Trace		Present
Anions present	Sulfate			Sulfate		Sulfate
Cations present	Sodium			Sodium		Sodium
QUANTITATIVE DETERMINATIONS						
Water	2.3	3.9	2.5	6.3	63.5	63.4
Alcohol-insoluble	53.1	10.1	59.9	13.6	.1	4.0
Fatty matter	3.1	1.4	2.1	1.6	.6	.4
Alkyl aryl sodium sulfonate ¹	41.5	84.6	35.5	78.5	35.8	32.2
Alkyl aryl sodium sulfonate, factor ²	11.9	23.7	10.0	20.9	9.0	8.4

¹ By difference.

² Milliliters of 0.1N sodium hydroxide required to neutralize reaction products of 1 gram of original material.

the iodine number (test 22) of the extracted fatty matter.

For materials containing mixtures of these soaps, the qualitative differentiation based on the Liebermann-Storch test and relative solubility in ligroine will be inconclusive and all the quantitative tests must be run for complete information.

Ammonium and amine soaps are often found in commercial admixtures and, since the ash will give no indication of these materials, tests must be made on the original admixtures to determine their presence. Ammonia, both in the free state and as ammonium salts, is detected by odor or a litmus paper test (test 2) and when present should be quantitatively determined (test 11). Amine soaps are indicated by a positive test for albuminoid nitrogen (test 1). Most soaps of this type are prepared with triethanolamine and this constituent can be quantitatively determined as the alcohol-insoluble portion of the dried aqueous extract after acidification (test 34). The weighed residue should be the hydrochloride salt of triethanolamine and it can be confirmed by determining its melting point (test 8).

Synthetic Detergents

The materials included in the synthetic detergent group are mainly limited to the petroleum derived alkyl aryl sodium sulfonates where there is only one alkyl and one aryl group present. The aryl group is either a benzene or naphthalene ring and the alkyl group is usually obtained from a petroleum distillate such as kerosene. Large amounts of sodium sulfate and smaller amounts of sodium chloride and mineral oils are also usually present as a consequence of the processing techniques.

The materials of this type marketed as admixtures are similar to the household detergents used for laundering and dishwashing. They are sold both as solid products and in aqueous solutions. Six of the materials examined were of this type and the results of the tests made are given in table 3. Samples 12–15 were solids containing considerable sodium sulfate, sample 16 was an aqueous solution of an alkyl aryl sulfonate without inorganic salts, and sample 17 was an aqueous solution containing some sodium sulfate.

As indicated in table 1, these materials are characterized by solubility in both water and dilute acid solution. They usually have a characteristic petroleum odor. Organically bound sulfur and sodium in the alcohol-soluble extract (which can be detected by examining the ash of this extract) are also indications of the presence of these synthetics.

The determinations considered to be necessary for the basic evaluation of these materials include those of water content (test 24), fatty matter (test 19), inorganic chlorides and sulfates, and a determination of the alkyl aryl sodium sulfonate (tests 32 or 33). The direct determination of water content by the distillation method should always be used for these materials since the organic matter tends to be partially decomposed and volatilized at the temperature used in the oven-drying test. The fatty matter is a measure of free oils and other hydrocarbons which are present mainly as impurities resulting from the manufacturing process. When inorganic chlorides or sulfates are shown to be present by qualitative tests on aqueous solutions of the original material, they must be taken into account in calculating the alkyl aryl sulfonate by difference. The sulfate

Table 4.—Analyses of sulfonated lignin salts

	Identification number				
	18	19	20	21	22
CHARACTERISTICS					
Probable source.....	← Paper pulp byproducts (acid process) →				
Form.....	← Powdered solid →				
Color.....	← Tan →				
Odor.....	← Slightly pungent →				
QUALITATIVE TESTS					
Solubility:					
In water.....	← Soluble →				
In alcohol, xylene, and chloroform.....	← Insoluble →				
Permanganate test.....	← Decolorizes immediately →				
Aqueous solution:					
Compatibility with hydrochloric acid.....	← Compatible →				
Test for calcium.....	← Positive (predominant) →				
Test for sodium.....	← Positive →				
Test for potassium.....	← Positive →				
Test for chloride.....	Trace	← Positive →			
Test for sulfate.....	← Negative →				
Ash:					
Presence.....	← Present →				
Test for sulfate.....	← Positive →				
Test for calcium.....	← Positive →				
QUANTITATIVE DETERMINATIONS					
Water.....percent..	14.1	21.2	19.0	23.6	22.3
Calcium chloride.....do..	.5	35.5	27.5	35.0	57.3
Calcium lignosulfonate ¹do..	85.4	43.3	53.5	41.4	20.4
Methoxyl ²do..	9.4	8.8	9.5	9.4	7.8

¹ By difference. ² Based on calcium lignosulfonate content.

(usually the sodium salt) is insoluble in alcohol and thus an alcohol extraction (test 9) serves adequately to determine this constituent. However, sodium chloride is soluble in alcohol and it must be calculated by determining the chlorides present in the alcohol-soluble extract (test 17).

The accuracy of the result obtained for synthetic detergent computed by difference (test 32) suffers from all the deficiencies inherent in any such calculation. An alternate and more direct measure of the synthetic detergent is obtained by a fairly rapid volumetric procedure (test 33). In this method, the alkyl aryl sulfonate is made to react with paratoluidine hydrochloride, the product extracted with carbon tetrachloride and subsequently titrated with standard sodium hydroxide. The results are usually expressed as a factor, i.e., the milliliters of 0.1-normal sodium hydroxide required to neutralize the reaction product from 1 gram of sample. Expressed in this form, the results offer a reliable and precise means for determining the uniformity of different lots of the same material, but no comparison between different materials can be made and the exact percentage of the constituent cannot be calculated. However, if a standard sample of the material being examined is available, the solution can be standardized in terms of the standard and the results expressed as percentages.

Sulfonated Lignin Materials

The materials in the sulfonated lignin group are mainly the calcium salts of sulfonated lignin derived from the acid (sulfite) process of paper pulp manufacture. These materials are commonly referred to as calcium lignosulfonates. Some

commercially marketed materials also contain calcium chloride and small amounts of alkyl aryl sulfonates.

These materials are usually available as tan powdered solids and have a pungent odor reminiscent of wood pulp. Five of the admixtures examined were of this type and the results of the tests made on these materials are shown in table 4. Sample 18 was chiefly calcium lignosulfonate and water, while samples 19–22 contained considerable calcium chloride in addition to the lignosulfonate.

As indicated in table 1, these admixtures are characterized by a high solubility in water, and compatibility with dilute mineral acids. They are mostly insoluble in organic solvents. Since the sulfur is organically bound, the material gives a negative test for sulfate in aqueous solution, and a positive test in the ash after igniting at 600° C. This type of lignin-derived material is easily oxidized and, therefore, immediately decolorizes an acidified permanganate solution (test 7). As shown in table 1, this test is a basis for distinguishing between these materials and the alkyl aryl sulfonates which do not rapidly decolorize the permanganate solution.

The determinations considered necessary for the basic evaluation of these materials are those of moisture content (test 24), calcium chloride if present (test 14), and calcium lignosulfonate by difference (test 16). Even though the materials are usually solid powders, the water content is normally appreciable. Oven drying is not advisable because of the possible decomposition on heating, and therefore the distillation method is recommended. In this connection, triethylbenzene

has been suggested by some as the solvent to be used for these materials. However, this solvent was found to be undesirable in that its higher boiling temperature caused some decomposition resulting in much "frying" and "bumping" during the distillation. Toluene or xylene were found to be much more satisfactory. The water-soluble chloride ion is determined by titration with standard silver nitrate solution, and calculated as calcium chloride. Calcium lignosulfonate is then generally considered to be the difference.

This procedure, while adequate for materials from known sources, does not give complete information on new or unknown materials since inert ingredients, if present, would be included as calcium lignosulfonate. Thus, it is suggested that the methoxyl determination (test 23) could be applied to these materials in much the same manner as for the lignin-derived resins. While extensive data are not available, all the materials of this type examined had approximately the same methoxyl contents, based on the calcium lignosulfonates. When available, a spectrophotometer can be used to determine lignosulfonate (test 15). This procedure involves the use of nitric acid to oxidize the lignin-derived material, and the developed color is measured photometrically. However, this test was not made in the Bureau laboratory.

A number of the commercial admixtures of this type contain small amounts of alkyl aryl sulfonates. These small amounts are not detectable by the usual qualitative tests and the volumetric determination described for the synthetic detergents is not suitable. In cases where they are known or believed to be present, they can be determined spectrophotometrically by the methylene-blue method (test 31).

Salts of Sulfonated Hydrocarbons

The tests for salts of sulfonated hydrocarbons are applicable to alkali, ammonium, or amine salts of sulfonated hydrocarbons derived from petroleum. The materials considered here are those obtained from the so-called "petroleum sulfonates" which result from acid treatments during the petroleum refining processes. They have several adjacent benzene nuclei rather than a single benzene or naphthalene ring common to the synthetic detergents which have been considered as a separate group.

The only admixture examined which was classified as being of this type was sample 23, the results being shown in table 5. This was an aqueous solution of a proprietary material commonly referred to as a triethanolamine salt of sulfonated hydrocarbons. This type of material has been extensively used both as a concrete admixture and a cement additive.

These materials are somewhat similar to the soaps in their qualitative characteristics and therefore require somewhat the same determinations. They are soluble in water and show some incompatibility in acidified aqueous solutions. Usually, more highly acidified solutions are required to detect incompatibility than is required in the case of the soaps. As indicated in table 1, the presence of the organically bound sulfur in the hydrocarbon portion of the molecule is the best means of differentiation from the soaps.

Table 5.—Analysis of a sulfonated hydrocarbon salt

Sample 23	
CHARACTERISTICS	
Probable source	Petroleum refining
Form	Liquid
Color	Dark brown
Odor	Petroleum
QUALITATIVE TESTS	
Solubility in water	Soluble
Compatibility of aqueous solution with hydrochloric acid	Incompatible
Ash:	
Presence	Present
Test for sulfate	Positive (predominant)
Test for sodium	Positive
Test for potassium	Positive
Ammoniacal nitrogen	Negative
Albuminoid nitrogen	Positive
QUANTITATIVE DETERMINATIONS	
Solids	percent 12.5
Ash	do 2.4
Total fatty matter	do 6.8
Triethanolamine	do 4.2
Total nitrogen	do .5

The determinations considered necessary for the basic evaluation of these materials are essentially the same as for the soaps. These are a determination of moisture content (tests 24 or 25), an ash determination (test 12), and a determination of the total fatty matter (test 18). As is true for all the petroleum-derived materials, the distillation method for water content is generally preferred because of the volatility of some of the constituents, but for fairly dilute solutions, such as sample 23, where unusually small amounts of material must be used in the distillation method, this latter method is at a disadvantage. The ash is important in determining the amounts and types of metallic cations present. Since the triethanolamine salts are very frequently used, the test for albuminoid nitrogen (test 1) is especially important for these materials and should always be conducted even when a fair amount of ash is present. Where a quantitative determination of triethanolamine is indicated to be necessary, it is conducted in the same manner as for soap materials.

In the determination of the total fatty matter the procedure varies slightly from that used for the true soaps in that a high concentration of mineral acid must be maintained not only in the initial solution but also in the subsequent wash water. This is necessary because the organic sulfonic acids are appreciably soluble in pure water but are "salted out" from the acid solution. For sulfonated hydrocarbons from the same source, the amount of organically bound sulfur should maintain a substantially constant relationship with the total fatty matter, and thus the quantitative determination of these sulfonates, as measured by the sulfate in the ash (test 30), may be used as a supplementary test for gauging uniformity of supply.

Proteinaceous Materials

Admixtures considered in the proteinaceous materials group include salts of proteinaceous

acids, and glue or other proteins, any of which may be admixed with non-proteinaceous substances.

Three of the admixtures examined were classified as being of this type. The results of these analyses are given in table 6. Samples 24 and 25 were essentially aqueous solutions of the calcium salts of complex proteinaceous acids obtained from protein hydrolysis. Sample 26, while classified as a proteinaceous material because of its glue content, differed considerably from the other two. This material was found to be an aqueous solution of a glue-like proteinaceous material containing a large amount of an alkyl aryl sodium sulfonate along with small amounts of sodium sulfate and petroleum oil. All of these materials give a positive Biuret test (test 5), which is indicative of proteinaceous material.

The determinations considered necessary for the basic evaluation of these materials are those of moisture content (tests 24 or 25), ash (test 12), and total nitrogen (test 27). The nitrogen is conveniently determined by a modified Kjeldahl procedure and its presence in substantial amounts is characteristic of proteinaceous materials since proteins contain from 15 to 17.5 percent nitrogen. Any additional tests to be made will depend upon the particular nature of the material. A putrefactive odor, solubility in water, and the predominance of calcium in the ash is indicative of calcium salts of complex proteinaceous acids. If

this is the case, the quantitative determination of calcium in the ash is of value in determining the uniformity of different lots from the same source (test 13). The proteinaceous acids cannot be determined as such because of their complexity and, therefore, the total nitrogen content must suffice as an approximate measure of proteinaceous materials. If desired, the value for total nitrogen may be used to calculate the approximate protein content of the sample by the use of an empirical factor (test 28).

Those admixtures containing glue along with other materials (as exemplified by sample 26) must be analyzed in a much different manner than the former proteinaceous materials. The glue portions of these materials are relatively insoluble in cold water, alcohol, and chloroform. Their solubility increases somewhat in hot water or hot alcohol. There are two tests by which glue can be qualitatively indicated (tests 3 or 4). These tests are based on the precipitation of glue with tannic acid or molybdate ion.

A quantitative estimation of the glue can be made by an empirical method (test 21). This procedure assumes an average nitrogen content for all animal glue. Therefore, the total nitrogen multiplied by the average factor gives the approximate amount of glue. The loss in weight obtained by igniting the dried alcohol-insoluble material can also be considered glue when it is known that no other organic alcohol-insoluble material

Table 6.—Analyses of proteinaceous materials

	Identification number		
	24	25	26
CHARACTERISTICS			
Probable source	← Hides →		Hides and petroleum
Form	← Liquid →		
Color	← Brown →		
Odor	← Putrefactive →		Petroleum
QUALITATIVE TESTS			
Solubility:			
In water	← Soluble →		Partially insoluble
In dilute hydrochloric acid	← Soluble →		Not determined
In chloroform	← Not determined →		Insoluble
Biuret test for proteinaceous materials	← Positive →		
Tests for glue	← Not determined →		Positive
Ash:			
Presence	← Present →		
Anions present	← Carbonate →		Sulfate
Cations present	← Calcium and sodium →		Sodium
QUANTITATIVE DETERMINATIONS			
Solids	percent 52.6	46.6	41.6
Ash	do 7.4	9.6	
Total nitrogen	do 6.8	5.4	2.3
Proteins ¹	do 42.8	34.0	
Alcohol-insoluble material	do		13.3
Ash from alcohol-insoluble material	do		1.5
Fatty matter	do		2.3
Glue-like material:			
Empirical ²	do		13.0
By difference	do		12.0
Synthetic detergent:			
By difference	do		26.3
Factor ³	do		6.0

¹ Total nitrogen × 6.3.

² Total nitrogen × 5.6.

³ Milliliters of 0.1N sodium hydroxide required to neutralize the reaction products of 1 gram of original material.

Table 7.—Analysis of an emulsifiable mixture

Sample 27	
CHARACTERISTICS	
Probable source.....	Petroleum
Form.....	Liquid
Color.....	Reddish brown
Odor.....	Petroleum
QUALITATIVE TESTS	
Compatibility:	
With water.....	Emulsifies
With chloroform, xylene.....	Soluble
With dilute hydrochloric acid.....	Incompatib'e
Ash:	
Presence.....	Present
Anions present.....	Carbonate
Cations present.....	& sulfate
	Sodium
QUANTITATIVE DETERMINATIONS	
Water..... percent.....	0.5
Ash..... do.....	2.1
Total fatty matter..... do.....	92.9
Unsaponified matter..... do.....	85.5
Soaps, by difference ¹ do.....	7.4

¹ Total fatty matter less unsaponified matter.

is present and when the inorganic salts are not volatilized during the ignition (test 20).

When alkyl aryl sulfonates are present along with glue, as was the case for sample 25, the examinations for this material can be conducted much the same as if alkyl aryl sulfonates alone were present. The alcohol-soluble portion will contain the alkyl aryl sulfonate plus any sodium chloride present, while the insoluble portion will contain the glue and the sodium sulfate. The volumetric method (test 33) for determining alkyl aryl sulfonates may be used for mixtures of this type.

Emulsifiable Mixtures

The materials included in the emulsifiable mixture group are those which contain chiefly unsaponifiable matter combined with sufficient soaps to form an emulsion when shaken with water. The soaps are usually sodium soaps of naphthenic acids but other types are possible.

Sample 27 was the only material of this type examined. The results of the tests made are given in table 7. This material was a mixture of a petroleum distillate in the lubricating oil range with sodium soaps of carboxylic acids

(probably naphthenic). This material and materials of the same type are characterized by their ability to form a substantially stable emulsion when shaken with water. The addition of hydrochloric acid will usually break the emulsion and produce a separate fatty layer. The original material is completely soluble in chloroform.

The determinations considered necessary for the basic evaluation of these materials are those of moisture content by the distillation method (test 24), ash (test 12), total fatty matter (test 18), unsaponified plus unsaponifiable matter (test 36), and soaps by difference. The amount of moisture in these materials is usually very low and would be present only as an impurity. The ash is useful in determining the extent and type of inorganic materials present. Total fatty matter extracted with chloroform from an acidified solution includes the soap acids and the unsaponified and unsaponifiable matter. A determination of unsaponified and unsaponifiable matter will then enable the calculation of the soap acids by difference. Generally the former material will be the unsaponifiable petroleum distillate, which is identifiable by its odor and appearance.

Usually the estimation of soaps (strictly speaking, soap acids) by difference is sufficient for this type of material but, if it is considered necessary, the acids from the soaps can be recovered by acidifying the alcohol-water phase after extracting the unsaponified and unsaponifiable matter, extracting with ligroine or ether (or chloroform where naphthenics or resins are suspected) and evaporating the solvent. The recovered material can then be examined qualitatively and quantitatively in the manner described for the soaps. For complete information, tests for albuminoid and ammoniacal nitrogen (tests 1 and 2) should be conducted on the original material, since nonmetallic soaps of this type may be present. When positive indications are obtained for either of these constituents, the quantitative determinations can be made in the same manner as described for the soaps (tests 11 or 27).

Soap-Forming Acids

The soap-forming acid group includes the various organic acids capable of being saponified to form soaps. The marketed material also usually contains some unsaponifiable matter.

Sample 28 was the only material of this type

Table 8.—Analysis of a soap-forming acid

Sample 28	
CHARACTERISTICS	
Probable source.....	Vegetable oils
Form.....	Paste
Color.....	Brown
Odor.....	Pungent
QUALITATIVE TESTS	
Solubility in water.....	Insoluble
Solubility in chloroform, ether, ligroine.....	Soluble
Ash.....	Trace
QUANTITATIVE DETERMINATIONS	
Water..... percent.....	0.4
Ash..... do.....	Trace
Unsaponifiable matter..... do.....	45.4
Total fatty matter..... do.....	99.6
Iodine No. (Wijs):	
On extracted fatty acids.....	30
On unsaponifiable matter.....	201

examined, the results of the tests made being given in table 8. It was derived from the processing of vegetable oils and fats and contained a mixture of fatty acids and unsaponifiable fatty constituents. This material and others of the same type are characterized by a negligible amount of ash, along with negative tests for ammoniacal and albuminoid nitrogen.

The determinations considered necessary for the basic evaluation of the materials are those of moisture content (tests 24 or 25), ash (test 12), and unsaponifiable matter (test 35). The water and ash determinations are considered necessary to show any large amount of impurities which may be present. When these determinations are made, it is usually considered unnecessary to evaluate the total fatty matter as such, since nominally the material is all fatty matter. A determination of unsaponifiable matter is important to show the extent to which non-soap-forming constituents are present. If the nature of the soap-forming acids is not known, they can be recovered from the alcohol-water phase after the extraction of the unsaponifiable matter. This recovered material can then be examined in the manner described for soaps. When the material is chiefly fatty acids, as in the case of sample 28, the iodine number of the fatty acids (test 22) can be used as a measure of the uniformity of different lots of the same material.

Appendix I.—Derivation of Admixtures from Industrial Processes

Petroleum Industry Products

The air-entraining admixture materials which were determined to be wholly or in part derived from the petroleum industry fall into three general categories: the naphthenates, the salts of sulfonated hydrocarbons, and the alkyl aryl sulfonates.

Naphthenic acids

Naphthenic acids are present in petroleum in small amounts, ranging from 0.1 to 3 percent. They are separated during the refining of various petroleum fractions such as ligroine (benzine), kerosene, and lubricating oil. These petroleum fractions are treated with strong sulfuric acid to remove aromatic and

unsaturated compounds. After separating the bulk of the acid sludge, the residual oily layers are subjected to a dilute caustic soda wash which results in the formation and solution of sodium naphthenates (soaps of naphthenic acid). The aqueous layer containing these soaps is separated and used as wetting or emulsifying agents alone or incorporated with various lubricants to form special cutting or emulsifiable oils. Commercial products representing both types of such materials have been marketed as air-entraining admixtures. Chemically, the naphthenic acids are classified as cyclo-paraffins, characterized by a saturated five- or six-membered carbon ring associated with a carboxylic acid group ($-\text{COOH}$). The alkali soap of this acid has an alkali metal (usually sodium or

potassium) substituted for hydrogen in the group ($-\text{COONa}$).

Sulfonated aromatic hydrocarbons

The second category of materials derived from the petroleum industry is the sulfonated aromatic hydrocarbons (or petroleum sulfonates). These materials are obtained during the refining of lubricating and white oil stocks with highly concentrated sulfuric acid. For example, in the preparation of white mineral oil for medicinal purposes, the stock oil is repeatedly treated with fuming sulfuric acid to remove substantially all the aromatic constituents in order to obtain the required colorless white oil. As a result of the high degree of sulfonation obtained in

the acid treatment, considerable amounts of aromatic sulfonic acids are produced (13). These acids are principally of two types—the so-called water-soluble type predominantly contained in the lower acid sludge, and the so-called oil-soluble type predominantly found in the upper oil layer of the reaction mixture. The water-soluble acids found in the sludge impart a dark green color to their aqueous solution and are consequently referred to as “green” petroleum sulfonic acids. The acids left in solution in the oil impart a reddish color to the oil and for this reason are generally referred to as “mahogany” petroleum sulfonic acids.

After the separation of the oil layer from the acid sludge, the oil layer is washed with aqueous alcohol solutions to extract the free oil-soluble sulfonic acids, or neutralized with alcoholic alkali and the sulfonates extracted as their alkali salts. These materials are used primarily as emulsifying agents and have been proposed for use as anti-stripping agents in bituminous mixtures (13).

The water-soluble or “green” petroleum sulfonic acids are recovered from the acid sludge as their salts by a process of water-washing, neutralization, and alcoholic extraction. They are used primarily as inexpensive detergents and wetting agents and particularly as a base for air-entraining admixtures for concrete and asphalt emulsion stabilizers (13). Chemically, the water-soluble sulfonic acids are characterized by having a complex ring structure consisting of several aromatic and one saturated ring nuclei associated with one or two sulfonic acid groups ($-SO_3H$). In one patent, a condensed petroleum sulfonic acid is combined with a hydroxyl-alkylamine (e.g., triethanolamine) which replaces one half of all the available hydrogen in the sulfonic acid groups to form a salt useful as a cement additive or concrete admixture (14).

Alkyl aryl sulfonates

The third type of admixture derived from the petroleum industry is the alkyl aryl sulfonates. While in the broadest sense these materials are also sulfonated hydrocarbons, their manner of derivation and their characteristics differ widely from the group previously discussed. These materials cannot be strictly classified as byproducts since they are manufactured by a direct synthesis. They are commonly referred to as synthetic detergents and have found a wide acceptance under various trade names as household and industrial detergents. They are usually prepared by chlorinating the kerosine fraction of petroleum distillates, condensing this product with an aromatic hydrocarbon (e.g., benzene or naphthalene), and sulfonating the aromatic portion of the complex with fuming sulfuric acid. This procedure produces a complex material consisting of a central aryl (aromatic) nucleus associated with two separate side groupings. One grouping is the alkyl side chain (hydrocarbons from the kerosine fraction) and the other is the sulfonic acid group ($-SO_3H$). The product is then neutralized with aqueous sodium hydroxide to form the alkyl aryl sodium sulfonate where the sodium ion replaces hydrogen in the sulfonic acid group to form the salt ($-SO_3Na$).

It is this complex organic salt which comprises the active ingredient of this type of synthetic detergent. As a result of the presence of sulfuric acid at the time of the alkali neutralization, a substantial amount of sodium sulfate is also formed. In many applications this salt is not removed since it increases the detergency of the product. Various dry formulations vary from 85 percent alkyl aryl sodium sulfonate and 15 percent sodium sulfate to 40 percent alkyl aryl sodium sulfonate and 60 percent sodium sulfate (15). The material is also marketed in aqueous solutions for air-entrainment purposes. The alkyl aryl sulfonates are sometimes added in small amounts to other types of concrete admixtures to enhance their ability to entrain air.

Paper Pulp Manufacture Products

There are two general types of processes used in the manufacture of paper pulp, both of which yield byproducts suitable as such or as a base for concrete admixtures—the acid process (sulfite) and the alkaline process (sulfate and soda).

Acid process

In the acid process the wood chips are digested under pressure in a solution of sulfurous acid and calcium acid sulfite. This digestion leaves the cellulose of the wood unaffected but decomposes the lignin and complex carbohydrates originally present. After a suitable digestion period the sulfite liquor is drawn off, leaving the cellulose pulp. The sulfite liquor contains about 8 to 14 percent solids which consist of approximately 60 percent calcium lignosulfonate, 20 percent reducing sugars, and 10 percent carbohydrates, the remainder being volatile acids, methyl alcohol, acetone, and inorganic impurities (16). The sulfite liquors have been used directly as admixtures for concrete. The liquor is also utilized for the production of alcohol by fermenting the sugars present. Following this fermentation, or as a separate process, the liquor may be treated with excess lime in order to obtain calcium sulfite which is returned to the digestion process. The basic calcium lignosulfonate resulting from the latter operation is removed as a filter cake and pressed to reduce its moisture content to about 50 percent.

The calcium lignosulfonate thus obtained and further dried exhibits excellent dispersing properties and is used to some extent as an admixture for concrete. In one patent an admixture is described which consists mainly of the solid residue of waste sulfite liquors after they have been fermented and the alcohol removed (17). Undoubtedly, the major portion of these solids is calcium lignosulfonates with most or all of the sugars removed. Chemically the lignosulfonate is believed to be a polymerized material made up of numerous benzene rings with hydrocarbon side chains, methoxyl ($-OCH_3$) groups, hydroxyl ($-OH$) groups, and calcium sulfonate groups.

Alkaline process

There are two major methods of alkaline digestion of wood for pulp manufacture—the soda and sulfate processes. In the former, the wood chips are digested with sodium hydroxide, while the latter process makes use of sodium sulfate in combination with sodium sulfide. The “black liquors” obtained in both cases are somewhat similar and have been used as such or with some refinement and modification as air-entraining admixtures for concrete.

The black liquors consist of a mixture of sodium salts of straight chain carboxylic acids, resin acids (predominately abietic), sterols, alcohols, unsaponifiable matter, and inorganic salts. The crude soap skimmings from the raw liquor may be used as an emulsifier (18). The active materials serving this purpose are primarily the sodium soaps of the fatty and resin acids. The black liquors are also refined to yield such products as tall oil, rosin and rosin soaps, turpentine, wood alcohol, and lignin. Tall oil and rosin are used as additional sources of air-entraining admixtures. Crude tall oil is the residue obtained by evaporating the sulfate liquor and acidifying the thick curds. It is an oily resinous mixture containing 30 to 59 percent fatty acids, 34 to 64 percent resin acids, and 5 to 10 percent unsaponifiable matter (19). Soaps usable as admixtures can be formed by reaction of the original tall oil with an alkaline substance (e.g., caustic soda, ammonia, etc.). Rosin and fatty acids may be separated from the tall oil and these can be saponified to produce a wetting agent (20). Lignin isolated from these liquors also has been recently contemplated for use as a dispersing agent.

Wood Stump Processing Products

In connection with the manufacture of naval stores, pine tree stumps which have been aged in the ground for about 10 to 15 years have been found to be an economical source of turpentine, pine oil, rosin, and other special resins. These latter resins are of a lignin nature, and when neutralized have been widely used for air-entrainment purposes.

The methods used for processing wood stumps vary considerably. One patented procedure (21) makes use of a coal tar hydrocarbon (such as benzene, toluene, etc.) to extract the wood chips. If the chips have not been previously steamed, the extract will contain turpentine, pine oil, FF-grade rosin and other resins. The extract is drawn off and the solvent recovered by

distillation. The distillation is continued to remove turpentine and pine oil. The residue, a solid containing rosin and other resins, is then dissolved in a mixture of a light petroleum hydrocarbon such as gasoline and some other suitable solvent such as furfural. The two solvent layers separate upon cooling. Rosin is obtained from the petroleum solvent and the resins are obtained from the furfural solvent. After removal of the solvent, the dried resin may be neutralized with sodium hydroxide to produce a sodium resinate which is used extensively as an air-entraining admixture for concrete. The structural chemistry of the original resin is not well developed. It is believed to be mainly of a lignin nature containing methoxyl ($-OCH_3$) and hydroxyl ($-OH$) groups as well as oxidized resin acids, oxidized terpenes, polyphenols, and polymerized terpenes (22). The empirical formula of the main constituent in the resin has been reported to be approximately $C_{27}H_{30}O_5$ and to have an average molecular weight of about 450 (23). The unneutralized resin is soluble in alcohol and coal tar solvents, but substantially insoluble in petroleum solvents and water.

Animal Hide Industry Products

Animal skins are mainly composed of proteins which nature utilizes as emulsifying agents. Thus, many byproducts incidental to the manufacture of leather also have good emulsifying properties and have been used as air-entraining admixtures.

Prior to tanning, the hides are dried, treated with a preservative (usually sodium chloride), and shipped to the tannery. The skins are then soaked in water to remove the preservative and soften the hide. This treatment also results in the solution of certain proteins and their degradation products (such as albumen). Degraded albumen contains lysalbinic and protalbinic acids which, when neutralized with some alkaline material, become useful as dispersing agents (24). After removing the areolar tissue, the skin is subjected to a lime-water treatment in order to hydrolyze and remove the keratinous proteins (the hair, nails, and horns of the epidermis). This results in the solution of calcium salts of complex amino acids which are also useful as dispersing agents. In addition, some of the albumen that was unaffected by the earlier water treatment is hydrolyzed and dissolved to yield more calcium salts of lysalbinic and protalbinic acids.

Gelatin, or glue, derived directly from the alkaline treatment of animal hides, is an excellent emulsifying and dispersing agent and has been used as a major ingredient in preparing commercial admixtures for concrete. One patent describes a mixture of animal hide glue and alkyl aryl sulfonate salt as being particularly suitable for producing cellular concrete (25).

Proteins are complex organic materials composed of units of amino acids having the general formula $NH_2-R-COOH$, where R stands for a complex carbon chain, and NH_2 and $COOH$ the amino and carboxylic acid groups, respectively. Animal glues are merely colloidal suspensions of protein molecules in water.

Fat and Vegetable Oil Processing Products

Animal and vegetable fats and oils are hydrolyzed by various methods to produce fatty acids. The raw fats and oils derived from animal and vegetable matter may be hydrolyzed at high pressure with lime or magnesia, or they may be processed by the use of sulfuric acid and an aromatic hydrocarbon such as naphthalene. The crude fatty acids so produced may then be distilled under vacuum to separate the individual acids.

Chemically, the fatty acids are characterized by a long hydrocarbon chain which is combined with a carboxylic acid group ($-COOH$). When saponified with an alkali, the fatty acids are converted to conventional soaps. These soaps are, of course, the most widely used of all wetting agents and detergents, and are sometimes used as admixtures for entraining air in concrete. Fatty acid soaps are also sometimes found combined with other type materials in commercial admixtures either purposefully or as a natural result of processing.

Appendix II.—Test Procedures

Many of the tests referred to in the preceding text are standard procedures and are given in the American Society for Testing Materials (A.S.T.M.) Book of Standards and other publications. Others are modifications of standard procedures or tests developed during the course of this work, while still others are non-standard tests suggested by the literature. In this appendix, all of these tests are numbered and are listed alphabetically according to the constituent being determined or according to the usual designation for the test. Qualitative and quantitative tests are given under separate headings.

For the standard tests and such tests where only minor modifications were made, the A.S.T.M. Book of Standards (26) designation is given along with a statement of the modification if any. For all tests not included in the A.S.T.M. Book of Standards, the basic procedures, reagents, and equipment are given, with references to the original sources when available.

Qualitative Tests

(1) *Albuminoid nitrogen (amines, etc.)*.—After boiling the material for several minutes as shown in the test for ammonia (test 2), cool the flask and its contents to room temperature, add an alkaline solution of potassium permanganate, boil, and test the vapors with moistened red litmus paper. A blue coloration is indicative of the original presence of albuminoid nitrogen.

(2) *Ammoniacal nitrogen (ammonia, etc.)*.—Place a small amount of the sample in a small narrow-mouthed flask. Add distilled water if necessary. If the sample is acid to methyl orange, add sufficient magnesium oxide to make alkaline. Boil and test the vapors with moistened red litmus paper. A blue coloration indicates the presence of free ammonia, ammonium soaps or salts.

(3) *Glue (tannic acid test)*.—Boil several grams of the material with 10–15 ml. of water for a few minutes. Filter while hot and cool to room temperature. To a portion of the filtrate add an equal volume of a cold 10-percent solution of sodium chloride nearly saturated with tannic acid and freshly filtered. A pale grayish-yellow flocculent precipitate indicates the presence of glue.

(4) *Glue (molybdate test)*.—To a portion of the cool water extract obtained in test 3, add half its volume of neutral ammonium molybdate solution followed by a few drops of nitric acid. The formation of a white amorphous precipitate indicates the presence of glue.

(5) *Proteinaceous matter (Biuret test)*.—Mix about five drops of the original sample in solution with approximately 3 ml. of reagent consisting of one part of 3-percent cupric sulfate solution and forty parts of 10-percent sodium hydroxide solution. A violet to purple coloration is indicative of a proteinaceous material.

(6) *Rosin (Liebermann-Storch test)*.—Use A.S.T.M. Method D 803-51, sections 57 and 58 (1952, Part 4, p. 672). This test should be run on the extracted and dried organic acids or fatty matter. A fugitive violet coloration is indicative of the presence of rosin or rosin acids.

(7) *Sulfonated lignin (permanganate test)*.—Dissolve a small amount of the material in 10 ml. of water, add 5 ml. of dilute sulfuric acid, and then a few drops of 0.5-percent potassium permanganate solution and shake. Where the color is discharged immediately, lignin is indicated.

(8) *Triethanolamine, melting point of the hydrochloride salt*.—The melting point of pure triethanolamine hydrochloride is 177°C. A melting point within the range of 173 to 181°C. is sufficient evidence of the presence of this compound.

Quantitative Tests

(9) *Alcohol-insoluble matter*.—Follow the procedure given by A.S.T.M. Method D 820-46, sections 10 and

11 (1952, Part 7, p. 607) except that the crucible and contents should be dried at 105°C. for several hours and weighed as alcohol-insoluble matter.

Where glue is known to be present, make the extraction at room temperature in a platinum or porcelain dish. After thorough stirring with each portion of alcohol, allow the insoluble matter to settle and filter the supernatant liquid through a fritted glass crucible. When the extraction is complete, return the contents of the crucible to the evaporating dish with a stream of 95-percent alcohol. Evaporate the alcohol on a steam bath and dry the contents of the dish to constant weight at 105°C. Weigh and calculate as the percentage of alcohol-insoluble matter in the sample.

(10) *Alcohol-soluble matter*.—Use A.S.T.M. Method D 820-46, sections 10 and 11 (1952, Part 7, p. 607).

(11) *Ammoniacal nitrogen*.—Weigh accurately 1 to 3 g. of sample into a 500-ml. distilling flask. Add 200 ml. of water and 2 g. or more of magnesium oxide free from carbonates. Connect the flask to the condenser with a Kjeldahl connecting bulb, distill 100 ml. of liquid into a measured quantity of standard acid (0.1N sulfuric acid recommended) and titrate with standard alkali solution (0.1N sodium hydroxide recommended) using methyl red as an indicator. The amount of standard acid to be added depends on the expected ammonia content of the sample. Calculate the result as the percentage of ammoniacal nitrogen present in the sample (ref. 27, method 2.27, p. 14).

(12) *Ash*.—Weigh sufficient sample into a small porcelain evaporating dish, dry over a steam bath, char and ignite to constant weight at 600°C. Calculate the results as the percentage of ash in the sample. If desired, the sample from the moisture determination (oven method) may be used for this test.

(13) *Calcium (in ash)*.—Analyze the material from the ash determination (test 12) for calcium by any suitable procedure (e.g., precipitation as oxalate, ignited and weighed as calcium carbonate or calcium oxide) after preliminary removal of silica and the ammonium hydroxide group. Express the result in terms of percentage of calcium in the ash.

(14) *Calcium chloride (Mohr's titration for chloride)*.—Weigh 1 g. of sample into a 300-ml. porcelain casserole, dissolve in 150–200 ml. of distilled water. Add 3 ml. of 5-percent potassium chromate solution and titrate with 0.1N silver nitrate solution. The end point is marked by the transition in color from a lemon yellow to a faint orange tinge which does not disappear on stirring. Standardize the silver nitrate solution with 0.1 to 0.2 grams of fused sodium chloride, titrated in the same manner as the sample. Express the result as the percentage of calcium chloride in the original sample.

(15) *Calcium lignosulfonate (colorimetric method)*.—Dissolve exactly 3.0 g. of sample in exactly 1 liter of water. Treat a 25-ml. aliquot of this solution with 5.0 ml. of concentrated nitric acid and dilute to exactly 50 ml. Measure the color developed by oxidation with nitric acid with a spectrophotometer at a wavelength of from 485 to 550 millimicrons and determine the concentration by use of a calibration curve prepared with a reference sample.

(16) *Calcium lignosulfonate (difference method)*.—Calculate the percentage of calcium lignosulfonate in the sample by subtracting the total of the percentages of calcium chloride, moisture, and synthetic detergent from 100.

(17) *Chlorides in alcohol-soluble matter*.—After the determination of fatty matter in synthetic detergent (test 19), use A.S.T.M. Method D 820-46, sections 19–21 (1952, Part 7, p. 610). Express the result as the percentage of sodium chloride in the sample.

(18) *Fatty matter (total)*.—Weigh accurately sufficient sample to yield about 1 g. of total fatty matter. Quantitatively transfer to a separatory funnel and dilute to 100 ml. with water. Acidify the material with sufficient hydrochloric acid to free all the fatty acids and extract with 75 ml. of chloroform. Follow with two more such extractions of 25 ml. each. Wash

the collected chloroform extracts twice with slightly acidified (HCl) water, distill or evaporate to a small volume, and then transfer to a small tared dish. Evaporate the residue to dryness and when free of chloroform, dry at 105°C. for 15-minute periods to constant weight. Calculate the result as the percentage of total fatty matter in the sample.

Note: When dealing with salts of petroleum sulfonates (sulfonated hydrocarbons), it will be necessary to use more strongly acidified solutions in order to reduce the solubility of the organic material in the aqueous phase. If desired, substantial amounts of sodium chloride in the aqueous phase will serve the same purpose.

(19) *Fatty matter in synthetic detergents*.—After the separation of the alcohol-soluble matter (test 10), determine as directed in A.S.T.M. Method D 820-46, sections 16–18 (1952, Part 7, p. 609).

(20) *Glue (from alcohol-insoluble matter)*.—After the determination of alcohol-insoluble matter (test 9), ignite the material at 600°C. and weigh. The loss in weight represents an approximation of the glue content, which is expressed as a percentage of the original material.

(21) *Glue (from total nitrogen)*.—Multiply the percentage of total nitrogen in the sample (test 27) by the factor 5.6 to obtain the percentage of glue present. See A.S.T.M. Method D 982-52, section 7c (1952, Part 7, p. 854). The factor 5.6 is an empirical relation based on an average nitrogen content for animal glues.

(22) *Iodine number (Wijs method)*.—Use the procedure given in A.S.T.M. Method D 460-46, section 38 (1952, Part 7, p. 592).

(23) *Methoxyl content*.—Use the A.S.T.M. Method C 114-51T, sections 2–4 (1952, Part 3, p. 102), except that the result shall be expressed as the percentage of methoxyl (OCH₃) present in the total fatty matter and that the determination shall be made on the material obtained as total fatty matter (test 18). In the case of solid samples, no previous extraction of total fatty matter is necessary, and is actually undesirable in the case of lignosulfonates. For the latter materials, the results should be expressed on the basis of the calcium lignosulfonate content. 1 ml. of 0.1N sodium thiosulfate solution is equivalent to 0.000517 g. of methoxyl (OCH₃).

(24) *Moisture (distillation method)*.—Use A.S.T.M. Method D 460-46, sections 11–13 (1952, Part 7, p. 584). Calculate the result as the percentage of moisture or water in the sample.

(25) *Moisture (oven method)*.—Use A.S.T.M. Method D 460-46, section 10 (1952, Part 7, p. 584). Calculate the result as the percentage of moisture or percentage of solids in the sample.

(26) *Naphthenic acids*.—Weigh accurately 3 to 5 g. of sample (or more if naphthenic acid content is less than 40 percent) into a 250-ml. conical flask. Add 25 ml. of alcohol (80 percent by volume) and reflux the mixture for 1 hour. Decant and save the extract and repeat the refluxing and decantation procedures with alcohol until the last extract does not leave a residue upon evaporation. Combine the extracts and evaporate to dryness on a steam bath. The residue consists of sodium naphthenates and other alcohol-soluble matter.

Dissolve the residue in water, transfer to a separatory funnel with the aid of wash water. Add an excess of copper sulfate solution (10 percent) to precipitate all the naphthenates as copper salts. Extract the material with benzene until a colorless extract is obtained. To ensure that sufficient copper is present, add more copper sulfate solution to the aqueous solution and again extract with benzene. If this extract is colored, add it to the combined benzene extracts. Wash the combined extracts with water, shaking lightly. Evaporate to dryness in a tared dish, dry for 1 hour at 105°C., cool, and weigh as copper naphthenate.

Weigh a portion of the dried copper naphthenate into a tared porcelain crucible, ignite gently with a

bunsen flame, cool, and weigh the residue as copper oxide. Calculate the copper content of the copper naphthenate (copper = 0.798 of copper oxide) in the ignited portion and use this factor to calculate the percentage of naphthenic acids in the sample (total weight of copper naphthenate less the weight of copper present divided by the weight of the sample).

Note: This method is based on that presented in the Institute of Petroleum standard methods (28). The term naphthenic acids as referred to here means the carboxylic acids occurring in crude petroleum which combine with copper to give benzene soluble salts.

(27) *Nitrogen (modified Gunning method)*.—Place 0.7 to 3.5 g. (according to nitrogen content) of dried sample in a Kjeldahl digestion flask. Add 30 ml. of concentrated sulfuric acid containing 1 g. of dissolved salicylic acid; shake until thoroughly mixed; and allow to stand at least 30 minutes or until complete solution results (shake frequently). Add 5 g. of sodium thiosulfate and heat gently for 5 minutes. Cool, add 10 g. of potassium sulfate or anhydrous sodium sulfate, and heat gently until foaming ceases. Slowly increase the heat until the acid boils and digest until the oxidation is complete, continuing for a time after the mixture is colorless or nearly so.

After cooling, dilute with approximately 200 ml. of water and add a few pieces of granulated zinc to prevent bumping, add sufficient sodium hydroxide solution (450 g. per liter) to make the reaction mixture strongly alkaline (50 to 100 ml. is usually sufficient), pouring it down the side of the flask so that it does not mix all at once. Connect the flask to the condenser by means of a Kjeldahl connecting bulb, taking care that the tip of the condenser extends below the surface of standard acid in the receiver. Mix the contents by shaking and distill until all ammonia has passed over into a measured quantity of the standard acid (amount of acid must be adjusted according to expected nitrogen content). The first 150 ml. of distillate usually contains all the ammonia. Titrate the excess of standard acid with standard alkali (0.1N NaOH) using methyl red as the indicator, and from the amount of acid consumed calculate the nitrogen content on the basis of the total sample.

Note: This method is essentially the same as a previously published procedure (ref. 27, method 2.26, p. 13).

(28) *Proteins*.—Multiply the percentage of total nitrogen as determined by test 27 by the factor 6.3 to obtain the percentage of proteins in the sample.

Note: This factor varies for different type proteins (from 5.6 to 6.7). However, 6.3 is considered to be of sufficient accuracy for the purposes of this estimation.

(29) *Rosin (McNicol method)*.—Follow the procedure in A.S.T.M. Method D 460-46, sections 29-32 (1952, Part 7, p. 589). Calculate the percentage of rosin on the basis of the original sample.

(30) *Sulfuric anhydride (organically combined)*.—Determine as directed in A.S.T.M. Method D 500-45, sections 23-26 (1952, Part 7, p. 632).

(31) *Synthetic detergent (colorimetric method)*.—Weigh accurately 1 g. of the sample. Dissolve and transfer to a 100-ml. volumetric flask. Fill to the mark. Measure an aliquot containing from 0.1 to 0.4 mg. of synthetic detergent into a separatory funnel and dilute to approximately 20 ml. with water. Neutralize the solution with dilute hydrochloric acid, using 3 to 4 drops in excess. Add 1 ml. of methylene blue solution (0.1-percent aqueous solution of methylene blue hydrochloride) and mix thoroughly. Add 20 ml. of chloroform, shake gently for 1 minute, let stand 5 minutes, and draw off the chloroform layer into a second separatory funnel. Add 20 ml. of distilled water to the second funnel and shake gently for 1 minute, let stand 5 minutes, and filter through cotton into a 100-ml. volumetric flask. Make three additional extractions with chloroform and subsequent washings as before. Wash the filter funnel and cotton with chloroform, fill the flask to mark with chloroform, mix, and analyze colorimetrically with a source of light at 652 millimicrons. The instrument should be standardized by using various sized aliquots of a solution of a reference sample of the synthetic detergent being determined, and utilizing the same procedure as described for the sample. Calculate the result as the percentage of synthetic detergent in the sample.

Note: This method is particularly applicable when the amount of synthetic detergent in the sample is small. Quantitative results are dependent upon the availability of a standard or reference sample for calibration purposes. The procedure has previously been published (29).

(32) *Synthetic detergent (difference method)*.—Calculate the percentage of synthetic detergent by subtracting the total of the percentages of moisture, alcohol-insoluble matter, fatty matter in synthetic detergent, and the chlorides (as sodium chloride) in the alcohol-soluble matter, from 100.

(33) *Synthetic detergent (volumetric method)*.—The method given here is adapted from a published procedure (30). It is based upon the principle that alkyl aryl sulfonates will react with p-toluidine hydrochloride in aqueous solution to form a complex amine salt which is soluble in carbon tetrachloride. Upon titration with standard alkali, the complex splits, yielding the organic sulfonic acid which reacts with the standard alkali. The results are expressed in terms of a factor, unless the molecular weight of the alkyl aryl sulfonate is known or a reference sample is available in which cases the percentage of synthetic detergent may be calculated directly. The determination is conducted as follows:

Weigh accurately 3 to 4 g. of solid sample (or suf-

ficient liquid sample to yield this amount of solids) into a 250-ml. separatory funnel. Add 50 ml. of carbon tetrachloride and 100 ml. of an aqueous solution containing 3.40 g. of paratoluidine hydrochloride. Stopper the funnel and shake for 5 to 10 minutes or until all the solid matter has disappeared. Let settle and draw off the carbon tetrachloride layer into a 500-ml. glass-stoppered Erlenmeyer flask. Repeat the extraction with 25 ml. of carbon tetrachloride.

Combine the extracts and add 100 ml. of 95-percent ethyl alcohol (just previously neutralized with 0.10N sodium hydroxide to a faint purple with m-cresol purple indicator solution). Titrate with standard 0.10N sodium hydroxide using m-cresol purple indicator (0.5 percent) until the emulsion formed by vigorous and intermittent shaking remains lavender. Express the results in terms of milliliters of 0.10N sodium hydroxide required to neutralize 1 g. of original sample.

Best results are obtained where the alkyl aryl sulfonate content of the solids is between 30 and 60 percent. The method is applicable to any compound containing an alkyl group combined with such aryl groups as benzene, toluene, phenol, or naphthalene.

(34) *Triethanolamine*.—The following procedure was devised by the authors and gave satisfactory results when other inorganic salts (especially sodium sulfate) were not present:

Weigh accurately a sample containing 1 to 2 g. solids into a 250-ml. beaker and dilute with water to 100 ml. Add sufficient concentrated hydrochloric acid to insure a moderate excess. Stir well and let settle (see note below). Decant the aqueous layer into a second beaker, taking care to retain all the undissolved material in the original beaker. Repeat the extraction with several 50-ml. portions of moderately acidified water.

Evaporate the combined extracts to dryness, add 100 ml. of 95-percent alcohol, stir well, and filter thru a tared fritted glass crucible of medium porosity. Wash the beaker and crucible with several portions of alcohol. Dry the crucible for one-half hour at 105°C., cool, and weigh as triethanolamine hydrochloride ($C_6H_{15}O_3N \cdot HCl$). Calculate the percentage of triethanolamine on the basis of the original sample (triethanolamine hydrochloride $\times 0.8033$ = triethanolamine).

Note: Where fatty matter separates and rises to the surface, it is advisable to carry out the extraction in a separatory funnel and draw off the aqueous layer.

(35) *Unsaponifiable matter*.—Use A.S.T.M. Method D 460-46, sections 25-27 (1952, Part 7, p. 589).

(36) *Unsaponified plus unsaponifiable matter*.—Use procedure shown in A.S.T.M. Method D 460-46, sections 22-24 (1952, Part 7, p. 588).

(37) *Unsaponified matter*.—Use A.S.T.M. Method D 460-46, section 28 (1952, Part 7, p. 589).

Appendix III.—References

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Admixtures Approved by the Bureau of Public Roads for Use on Direct Government Contracts in the National Parks and National Forests

Trade Name	Manufactured by	Trade Name	Manufactured by
Aerolith	L. Sonneborn Sons, Inc., New York, N. Y.	Pozzolith 8	Master Builders Co., Cleveland, Ohio.
Airalon AEA	Dewey & Almy Chemical Co., Cambridge, Mass.	Pozzolith 10A	Master Builders Co., Cleveland, Ohio.
Ayr-Trap #1	A. C. Horn Co., Long Island City, N. Y.	Protex AEA	Autolene Lubricants Co., Denver, Colo.
Ayr-Trap #2	A. C. Horn Co., Long Island City, N. Y.	Ricco	Richards Sales Corp., Jersey City, N. J.
Darex AEA	Dewey & Almy Chemical Co., Cambridge, Mass.	Santomerose No. 1	Monsanto Chemical Co., St. Louis, Mo.
Durair	Techkote Co., Inc., Inglewood, Calif.	Santomerose S	Monsanto Chemical Co., St. Louis, Mo.
Kutwell 40	Esso Standard Oil Co., New York, N. Y.	Sika AER	Sika Chemical Corp., Passaic, N. J.
Nacconol NR	Allied Chemical & Dye Corp., New York, N. Y.	Spray-O-Bond	Spray-O-Bond Co., Milwaukee, Wis.
Nacconol Z	Allied Chemical & Dye Corp., New York, N. Y.	Specs	E. L. Moore Co., Pasadena, Calif.
N-Tair	Newport Industries, Inc., New York, N. Y.	Ultrawet 30E	The Atlantic Refining Co., Philadelphia, Pa.
Portite	Hopper Products, Inc., New York, N. Y.	Ultrawet K	The Atlantic Refining Co., Philadelphia, Pa.
Pozzolith 4A	Master Builders Co., Cleveland, Ohio.	Veriset	Verapon, Inc., New York, N. Y.
Pozzolith 5A	Master Builders Co., Cleveland, Ohio.	Vinsol NVX	Hercules Powder Co., Wilmington, Del.

The admixtures included above are approved subject to the following provision: Either prior to or at any time during construction the engineer may require that the admixture selected by the contractor be further tested to determine its effect upon the strength of the concrete. When so tested, compressive strength at 7 days of concrete made with the cement and aggregates and in the proportions to be used in the work and containing the admixture under test in an amount sufficient to produce from 3 to 6 percent entrained air in the plastic concrete, shall not be less than 88 percent of the strength of concrete made with

the same materials and with the same cement content and consistency but without the admixture.

The percentage reduction in strength shall be calculated from the average strength of at least five standard 6- by 12-inch cylinders of each type of concrete. Specimens shall be made and cured in the laboratory in accordance with A.S.T.M. Standard Method of Making and Curing Concrete Compression and Flexure Specimens in the Laboratory, C 192-49, and shall be tested in accordance with A.S.T.M. Standard Method of Test for Compressive Strength of Molded Concrete Cylinders, C 39-49. The percentage of

entrained air shall be determined in accordance with A.S.T.M. Tentative Method of Test for Air Content of Freshly Mixed Concrete by the Pressure Method, C 231-49 T.

The contractor will be required to follow an approved procedure for adding the specified amount of air-entraining admixture to each batch and will be held responsible for its uniform operation during the progress of the work. The contractor shall provide separate approved scales for such admixtures as are to be proportioned by weight and accurate measures for such admixtures as are to be proportioned by volume.

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Annual Reports of the Bureau of Public Roads:

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Part 1.—Nonuniformity of State Motor-Vehicle Traffic Laws (1938). 15 cents.

Part 2.—Skilled Investigation at the Scene of the Accident Needed to Develop Causes (1938). 10 cents.

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UNIFORM VEHICLE CODE

Act I.—Uniform Motor-Vehicle Administration, Registration, Certificate of Title, and Antitheft Act (1945). 15 cents.

Act II.—Uniform Motor-Vehicle Operators' and Chauffeurs' License Act (revised 1952). 15 cents.

Act III.—Uniform Motor-Vehicle Civil Liability Act (1944). 10 cents.

Act IV.—Uniform Motor-Vehicle Safety Responsibility Act (revised 1952). 15 cents.

Act V.—Uniform Act Regulating Traffic on Highways (revised 1952). 20 cents.

Model Traffic Ordinance (revised 1952). 20 cents.

MAPS

State Transportation Map series (available for 39 States). Uniform sheets 26 by 36 inches, scale 1 inch equals 4 miles. Shows in colors Federal-aid and State highways with surface types, principal connecting roads, railroads, airports, waterways, National and State forests, parks, and other reservations. Prices and number of sheets for each State vary—see Superintendent of Documents price list 53.

United States System of Numbered Highways together with the Federal-Aid Highway System (also shows in color National forests, parks, and other reservations). 5 by 7 feet (in 2 sheets), scale 1 inch equals 37 miles. \$1.25.

United States System of Numbered Highways. 28 by 42 inches, scale 1 inch equals 78 miles. 20 cents.

MISCELLANEOUS PUBLICATIONS

Bibliography of Highway Planning Reports (1950). 30 cents.

Construction of Private Driveways, No. 272MP (1937). 10 cents.

Electrical Equipment on Movable Bridges, No. 265T (1931). 40 cents.

Factual Discussion of Motortruck Operation, Regulation, and Taxation (1951). 30 cents.

Federal Legislation and Regulations Relating to Highway Construction (1948). Out of print.

Financing of Highways by Counties and Local Rural Governments, 1931-41. 45 cents.

Highway Accidents (1938). 10 cents.

Highway Bond Calculations (1936). 10 cents.

Highway Bridge Location, No. 1486D (1927). 15 cents.

Highway Capacity Manual (1950). 65 cents.

Highway Needs of the National Defense, House Document No. 249 (1948). 75 cents.

Highway Practice in the United States of America (1949). 75 cents.

Highway Statistics (annual):

1945, 35 cents.	1948, 65 cents.	1952, 75 cents.
1946, 50 cents.	1949, 55 cents.	
1947, 45 cents.	1951, 60 cents.	

Highway Statistics, Summary to 1945. 40 cents.

Highways in the United States, nontechnical (1951). 15 cents.

Highways of History (1939). 25 cents.

Identification of Rock Types (1950). 10 cents.

Interregional Highways, House Document No. 379 (1944). 75 cents.

Legal Aspects of Controlling Highway Access (1945). 15 cents.

Local Rural Road Problem (1950). 20 cents.

Manual on Uniform Traffic Control Devices for Streets and Highways (1948). 75 cents.

Mathematical Theory of Vibration in Suspension Bridges (1950). \$1.25.

Principles of Highway Construction as Applied to Airports, Flight Strips, and Other Landing Areas for Aircraft (1943). \$2.00.

Public Control of Highway Access and Roadside Development (1947). 35 cents.

Public Land Acquisition for Highway Purposes (1943). 10 cents.

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Roadside Improvement, No. 191MP (1934). 10 cents.

Selected Bibliography on Highway Finance (1951). 55 cents.

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Standard Plans for Highway Bridge Superstructures (1953). \$1.00.

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DEPARTMENT OF COMMERCE - BUREAU OF PUBLIC ROADS
STATUS OF FEDERAL-AID HIGHWAY PROGRAM

AS OF DECEMBER 31, 1953

(Thousand Dollars)

STATE	UNPROGRAMMED BALANCES	ACTIVE PROGRAM											
		PROGRAMMED ONLY			PLANS APPROVED, CONSTRUCTION NOT STARTED			CONSTRUCTION UNDER WAY			TOTAL		
		Total Cost	Federal Funds	Miles	Total Cost	Federal Funds	Miles	Total Cost	Federal Funds	Miles	Total Cost	Federal Funds	Miles
Alabama	\$5,032	\$9,557	\$4,501	138.3	\$7,369	\$3,684	95.2	\$41,793	\$21,297	438.7	\$58,719	\$29,482	672.2
Arizona	1,283	1,894	1,267	57.4	52	47		6,748	4,762	85.9	8,694	6,076	143.3
Arkansas	2,352	9,179	5,045	325.1	5,524	2,754	123.1	9,257	4,664	212.5	23,960	12,463	667.7
California	1,452	4,965	2,827	52.8	3,907	2,169	12.9	92,358	44,474	217.2	101,230	49,470	289.9
Colorado	1,923	3,545	1,906	70.7	1,215	683	35.4	18,314	9,932	181.5	23,074	12,601	287.6
Connecticut	6,760	450	275	2.0	1,672	883	1.7	8,581	4,228	25.9	10,703	5,386	29.6
Delaware	791	4,877	2,462	28.7	355	177	6.3	3,599	1,792	18.8	8,831	4,431	53.6
Florida	4,327	11,454	5,797	157.9	7,308	4,000	136.6	18,766	9,657	262.7	37,528	19,454	557.2
Georgia	3,979	15,116	7,740	335.6	7,382	3,688	109.4	31,897	14,936	446.7	54,395	26,364	891.7
Idaho	2,117	5,757	3,595	92.2	3,386	2,127	41.5	9,067	5,665	158.6	18,210	11,387	292.3
Illinois	10,264	21,494	11,052	153.7	13,321	6,600	53.4	54,918	29,222	286.2	89,733	46,874	493.3
Indiana	11,656	28,168	15,432	133.4	9,205	4,617	45.4	16,710	8,870	53.3	54,083	28,919	232.1
Iowa	2,119	10,057	5,439	248.0	5,683	2,936	145.1	13,303	7,749	429.7	29,043	16,124	822.8
Kansas	2,777	9,905	4,956	790.4	2,756	1,392	293.2	13,423	6,554	657.6	26,084	12,902	1,741.2
Kentucky	1,779	9,609	5,148	108.7	5,483	2,741	79.4	20,918	10,974	203.5	36,010	18,863	391.6
Louisiana	2,264	15,862	7,930	122.0	4,621	2,340	37.2	26,997	13,064	141.9	47,480	23,334	301.1
Maine	1,050	4,077	2,176	27.1	760	380	4.7	11,265	5,644	84.7	16,102	8,200	116.5
Maryland	8,177	2,617	1,412	34.1	4,663	2,230	24.8	8,668	4,803	32.2	15,948	8,445	91.1
Massachusetts	4,951	1,543	906	6.4	7,159	3,562	10.3	40,415	18,710	23.9	49,117	23,178	40.6
Michigan	1,982	24,592	12,556	327.2	8,786	4,616	131.7	48,868	20,802	163.3	82,246	37,974	622.2
Minnesota	3,593	9,398	5,098	765.1	2,008	1,031	41.5	12,705	6,712	201.8	24,111	12,841	1,008.4
Mississippi	946	10,949	5,589	299.7	3,672	1,804	132.7	21,595	10,932	520.1	36,216	18,325	952.5
Missouri	5,568	13,435	6,814	763.7	4,867	2,510	153.1	48,114	22,921	336.4	65,016	32,247	1,253.2
Montana	3,819	11,362	6,958	258.9	4,803	2,893	96.1	15,728	9,525	248.4	31,893	19,376	603.4
Nebraska	6,228	22,629	11,763	682.6	4,306	2,371	104.8	8,562	4,872	227.5	35,497	19,006	1,014.9
Nevada	2,504	5,485	4,590	80.6	457	383	15.1	4,807	3,987	101.7	10,749	8,960	197.4
New Hampshire	2,727	1,780	890	10.1	1,084	537	3.6	4,272	2,254	25.2	7,136	3,681	38.9
New Jersey	2,779	5,769	2,859	56.2	1,834	877	5.1	30,651	14,654	24.9	38,254	18,390	86.2
New Mexico	566	1,284	794	38.2	2,163	1,374	45.9	9,443	5,911	204.8	12,890	8,079	288.9
New York	13,584	54,812	29,141	100.8	48,079	23,530	19.5	141,827	66,016	386.5	244,718	118,687	506.8
North Carolina	3,048	19,078	9,343	330.2	3,461	1,609	73.6	29,979	14,181	352.9	52,518	25,133	756.7
North Dakota	2,988	3,019	1,517	504.8	788	394	62.6	6,437	3,371	347.5	10,244	5,282	914.9
Ohio	2,605	21,678	7,888	125.2	12,758	6,506	37.4	75,916	36,198	88.9	110,352	50,592	251.5
Oklahoma	4,402	14,136	7,771	195.9	6,839	3,715	87.7	13,995	7,436	187.7	34,970	18,222	471.3
Oregon	813	452	266	6.5	3,461	1,957	55.9	9,189	5,568	134.8	13,102	7,791	197.2
Pennsylvania	3,591	13,425	5,479	4.1	24,965	12,183	44.0	79,384	38,923	156.1	117,774	56,585	204.2
Rhode Island	1,805	2,569	1,284	33.8	307	153		9,797	4,896	24.6	12,673	6,333	58.4
South Carolina	1,882	10,537	5,879	201.5	2,005	977	105.8	13,435	6,673	262.4	25,977	13,529	569.7
South Dakota	957	5,178	3,060	305.2	1,760	988	70.7	6,606	3,689	377.2	13,544	7,737	753.1
Tennessee	2,565	10,249	5,102	297.0	8,047	4,037	192.7	29,074	13,187	225.8	47,370	22,326	715.5
Texas	6,495	2,266	1,183	20.4	12,968	6,592	355.8	52,420	28,525	844.3	67,654	36,300	1,220.5
Utah	464	1,749	1,350	27.0	1,325	993	22.1	8,822	6,769	121.9	11,896	9,112	171.0
Vermont	536	3,216	1,727	33.5	296	148	5.5	6,043	3,067	27.4	9,560	4,942	66.4
Virginia	701	8,594	3,787	109.9	5,985	2,663	88.0	26,853	12,966	165.2	41,432	19,416	363.1
Washington	851	7,748	4,094	128.6	1,480	823	16.6	17,325	9,128	112.2	26,553	14,045	257.4
West Virginia	3,360	7,445	3,774	59.1	4,877	2,457	3.5	10,683	5,351	46.7	23,005	11,582	109.3
Wisconsin	2,075	9,402	5,088	130.2	3,521	1,805	91.4	20,907	10,562	169.8	33,830	17,655	391.4
Wyoming	429	605	390	12.6	1,031	666	22.8	7,193	4,506	127.2	8,829	5,562	162.6
Hawaii	1,173	3,054	1,495	4.8	343	169	3.0	9,818	4,686	12.3	13,215	6,350	20.1
District of Columbia	845	7,488	3,504	5.5	115	58	.8	12,538	5,779	2.2	20,141	9,341	8.5
Puerto Rico	3,487	10,561	4,865	51.9	617	234	2.1	12,939	6,187	40.1	24,117	11,286	94.1
TOTAL	164,421	494,070	255,844	8,862.3	270,829	138,063	3,346.7	1,251,527	627,231	10,236.3	2,016,426	1,021,138	22,445.3

